SHORT COURSE
Tools for Management of Chlorinated Solvent – Contaminated Sites

3 December 2009

DoD EPA DOE SERDP

ESTCP

Report Documentation Page

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Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

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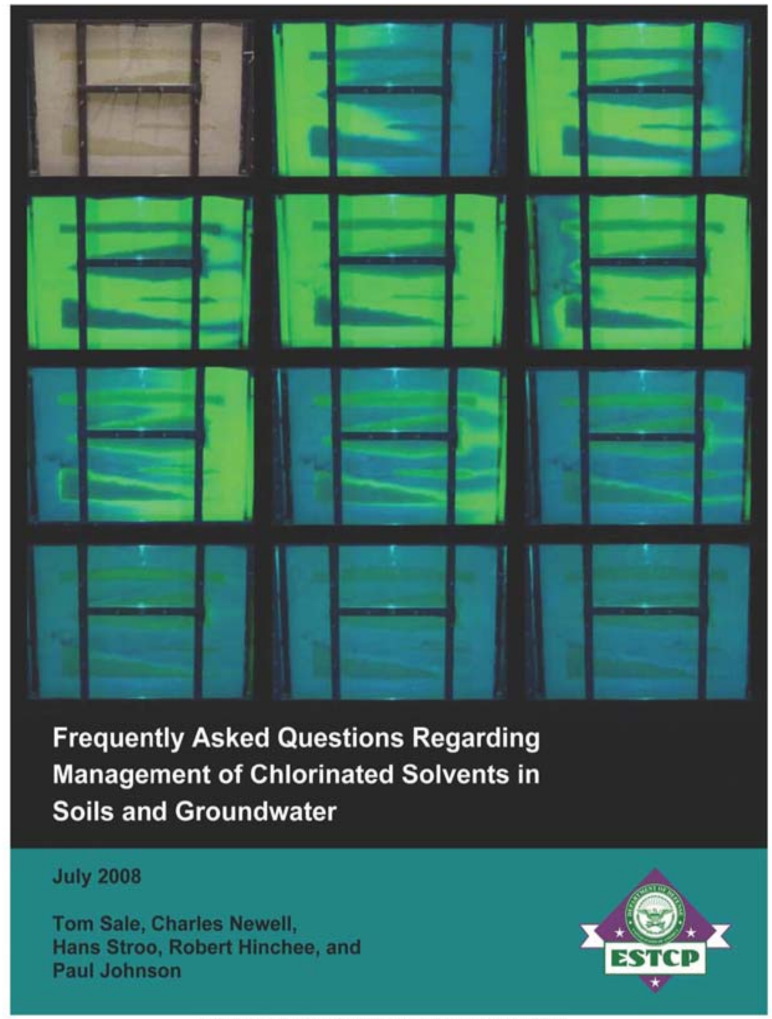
Guide for Selecting Remedies for Subsurface Releases of Chlorinated Solvents
ER-0530

Tom Sale, Chuck Newell,
Hans Stroo, Rob Hinchee, and Paul Johnson

Frequently Asked Questions

- Provides quick access to key concepts and references for those who need to know more

- August 2008
- Google - Chlorinated Solvents FAQs
- http://www.estcp.org/Technology/upload/ER-0530-FAQ.pdf



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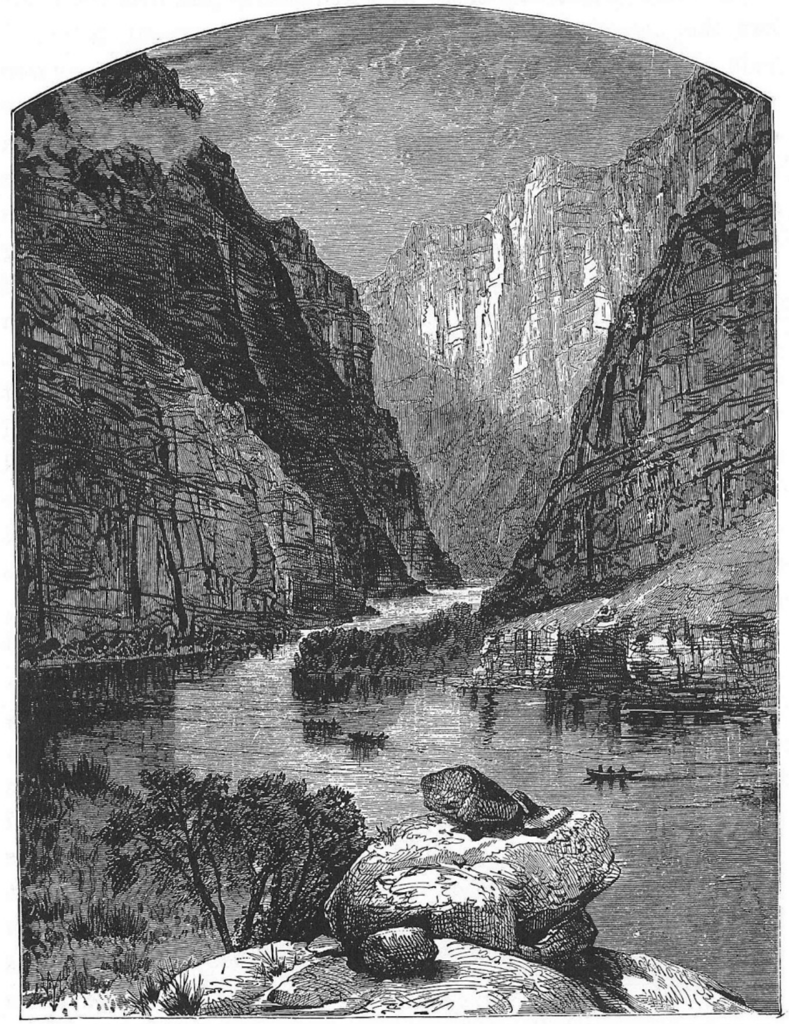
Decision Guide

- Supports
  - Understanding site specific conditions,
  - Developing goals,
  - Selecting technologies, and
  - Packaging site remedies



GATE OF LODORE.

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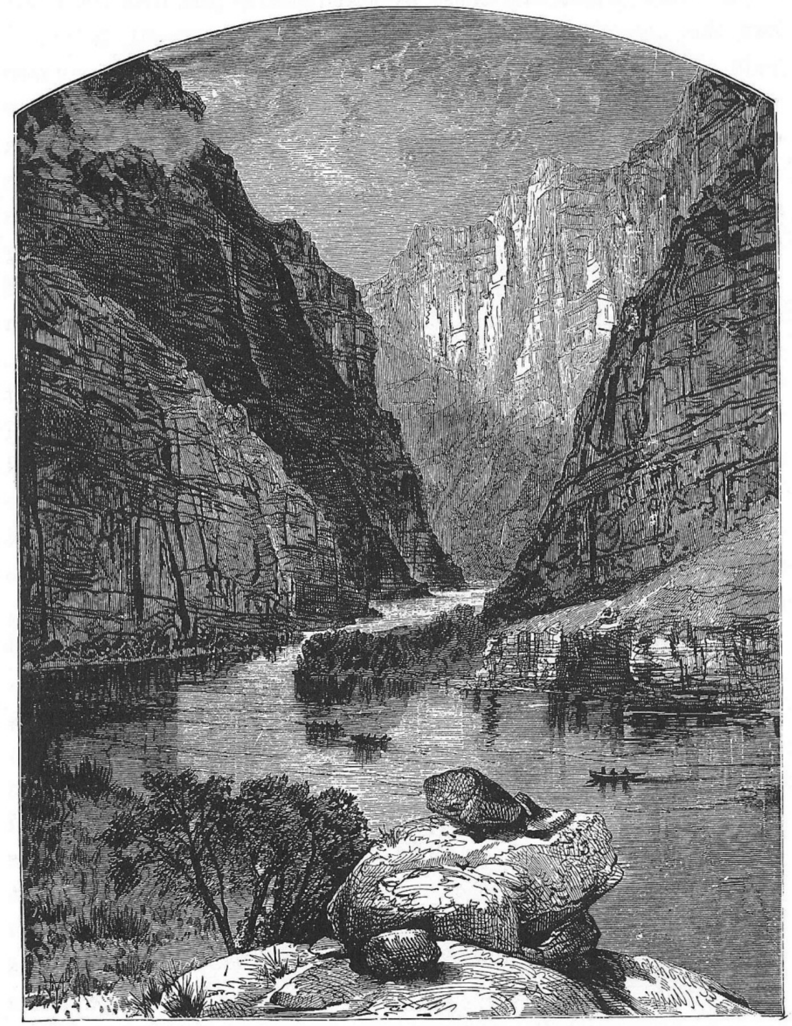
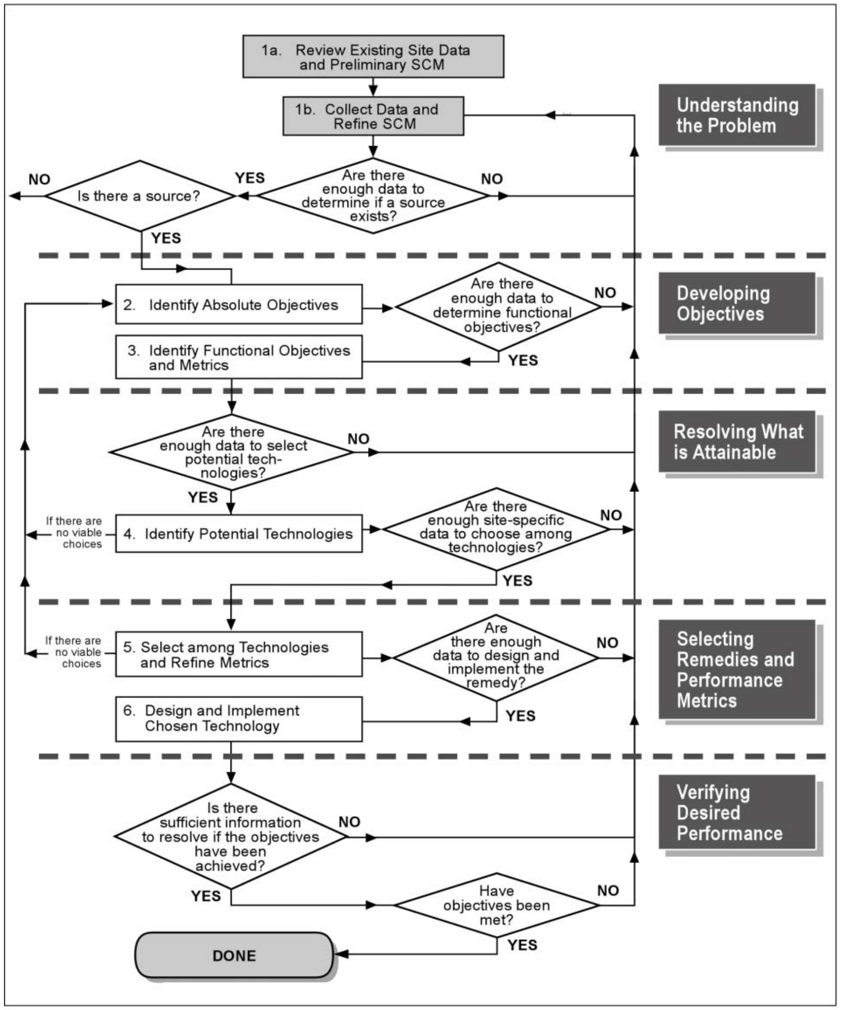


GATE OF LODORE.

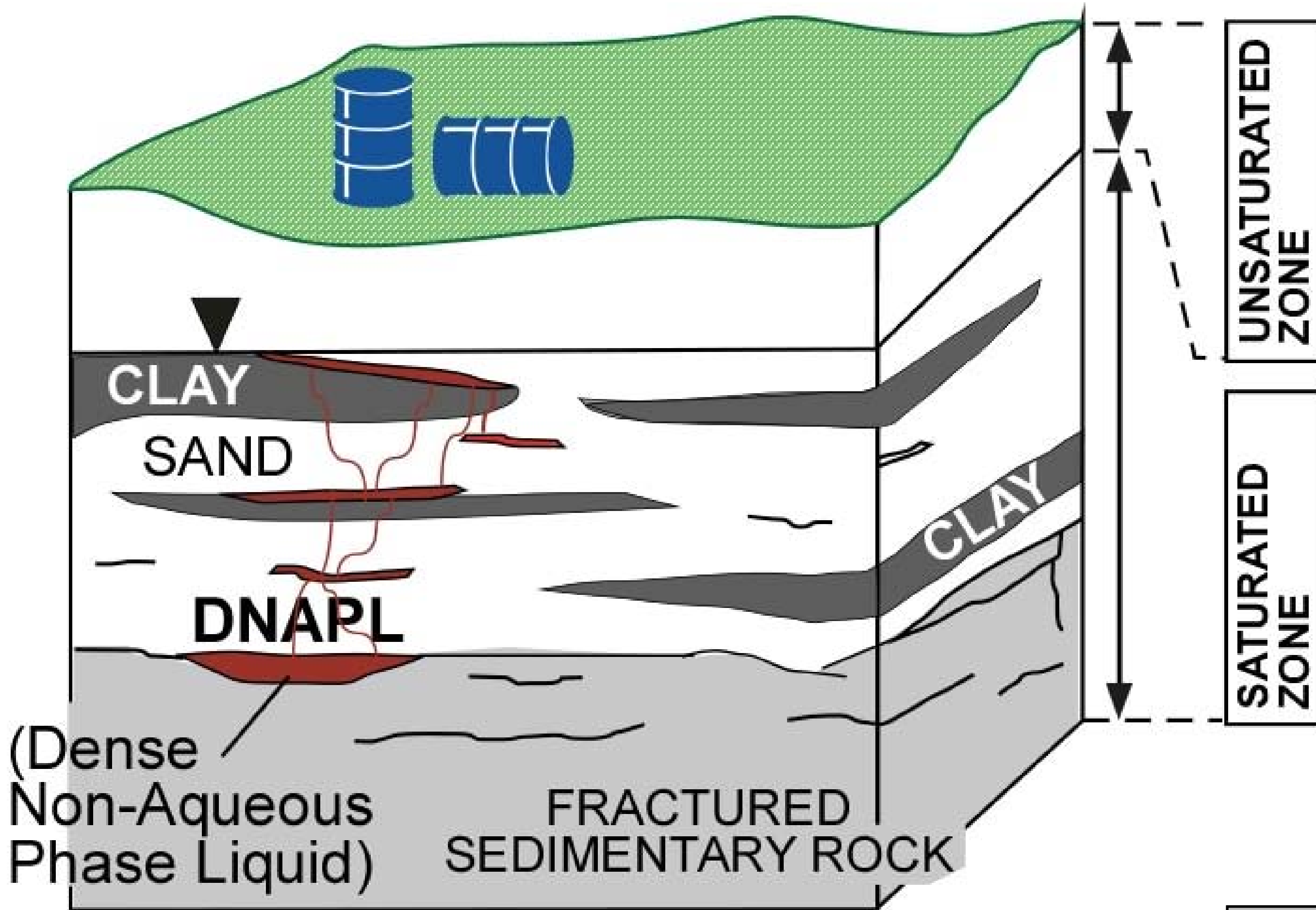
Following NRC 2005



Understanding site specific conditions

Inadvertent releases reflecting past practices…

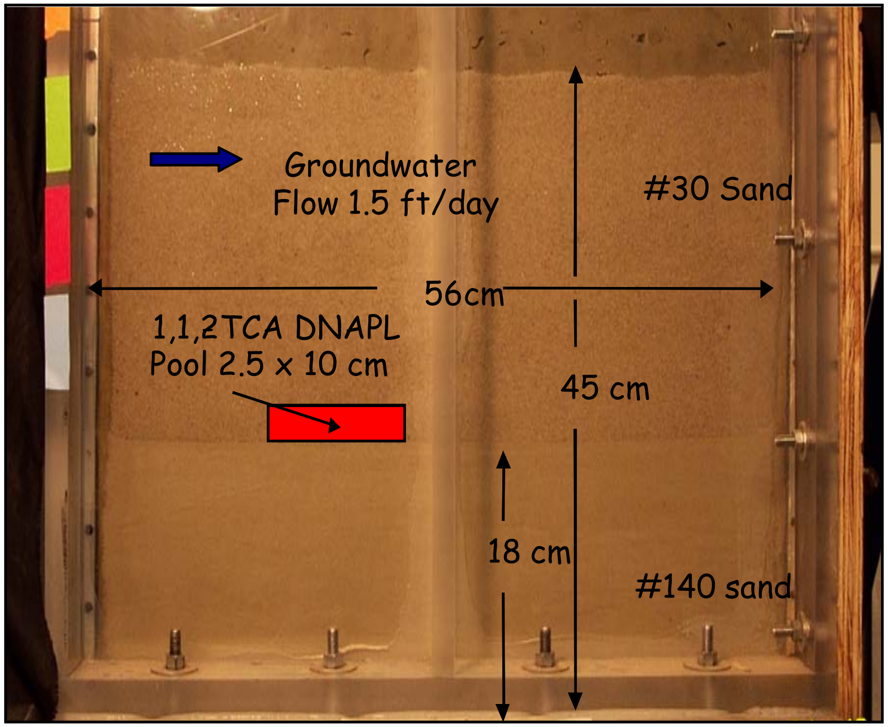
Early Stage

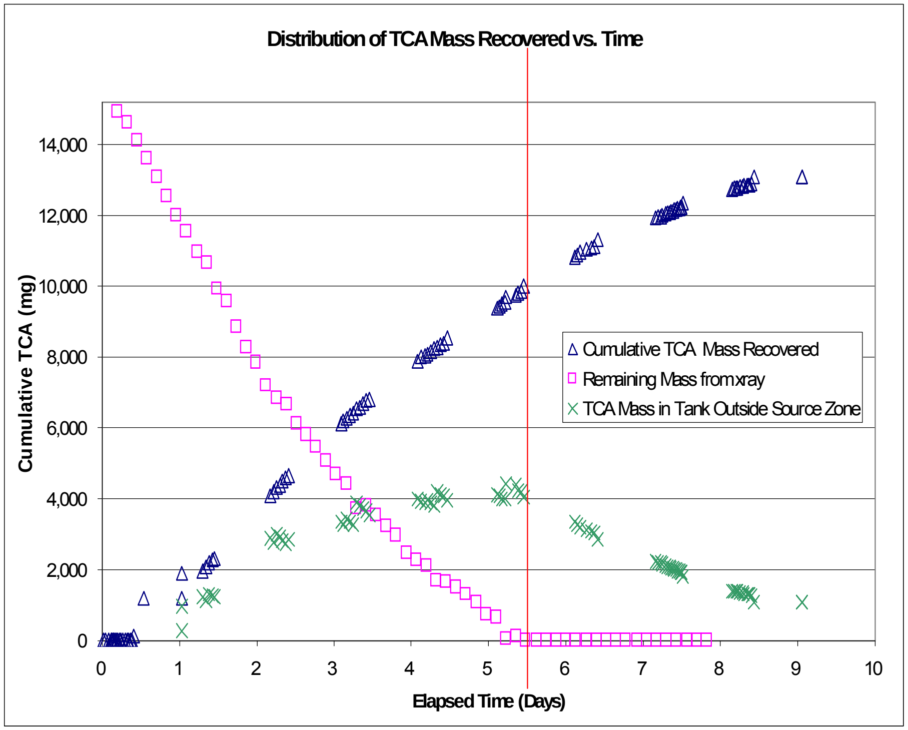


Sale et al., 2008

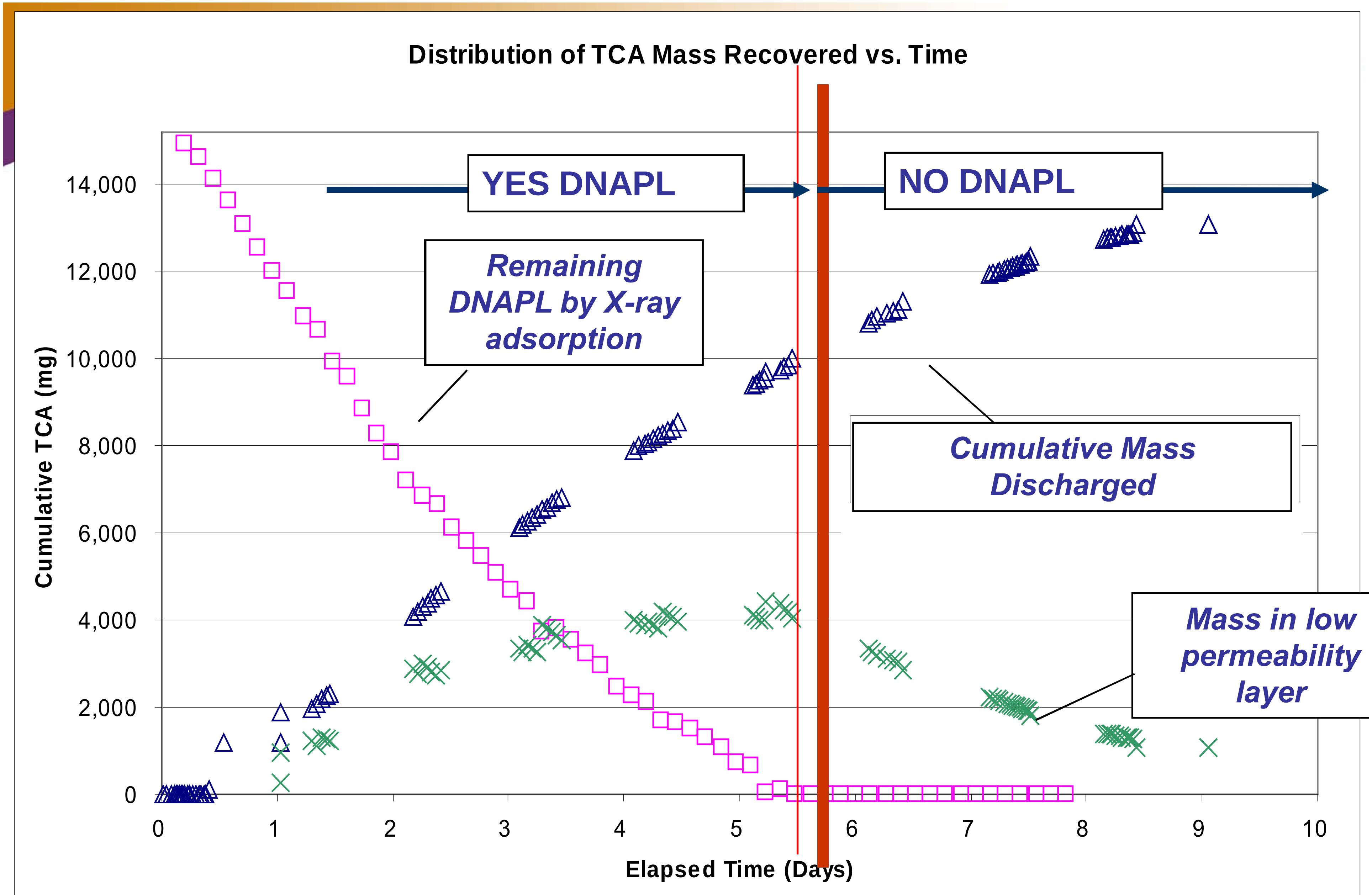
Two layer sand tank study

Colorado School of Mines (Tissa Illangasekare and Bart Wilkins)



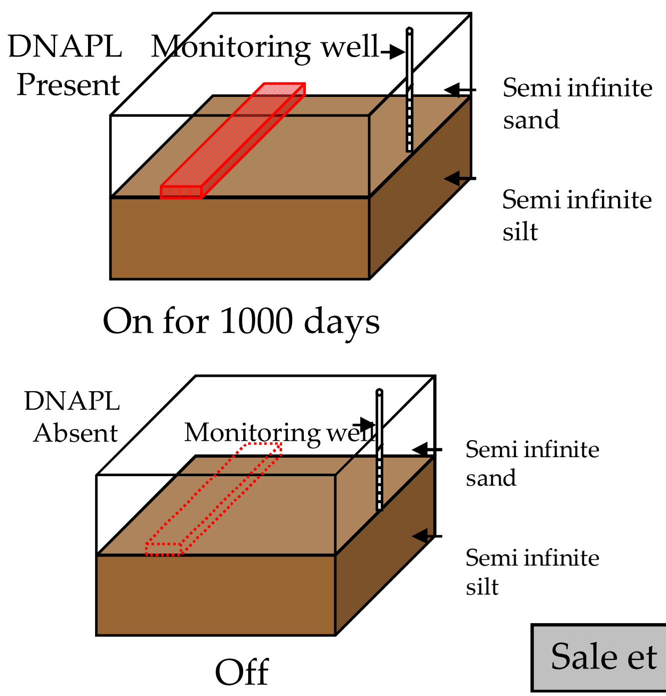


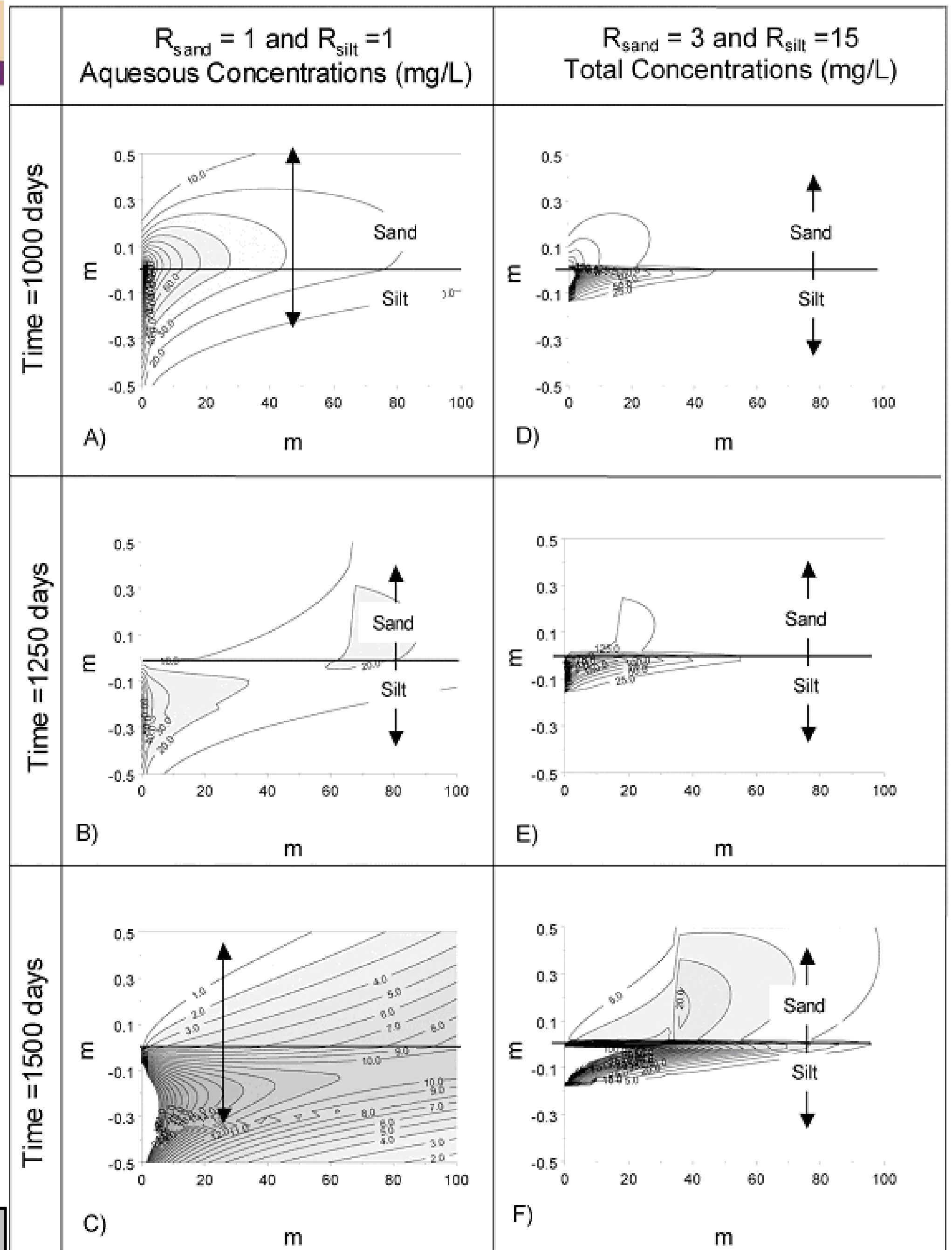
AFCEE Source Zone Initiative (2007)



AFCEE Source Zone Initiative (2007)

Aqueous and sorbed phases in transmissive and low permeability zone





Sale et al., 2008

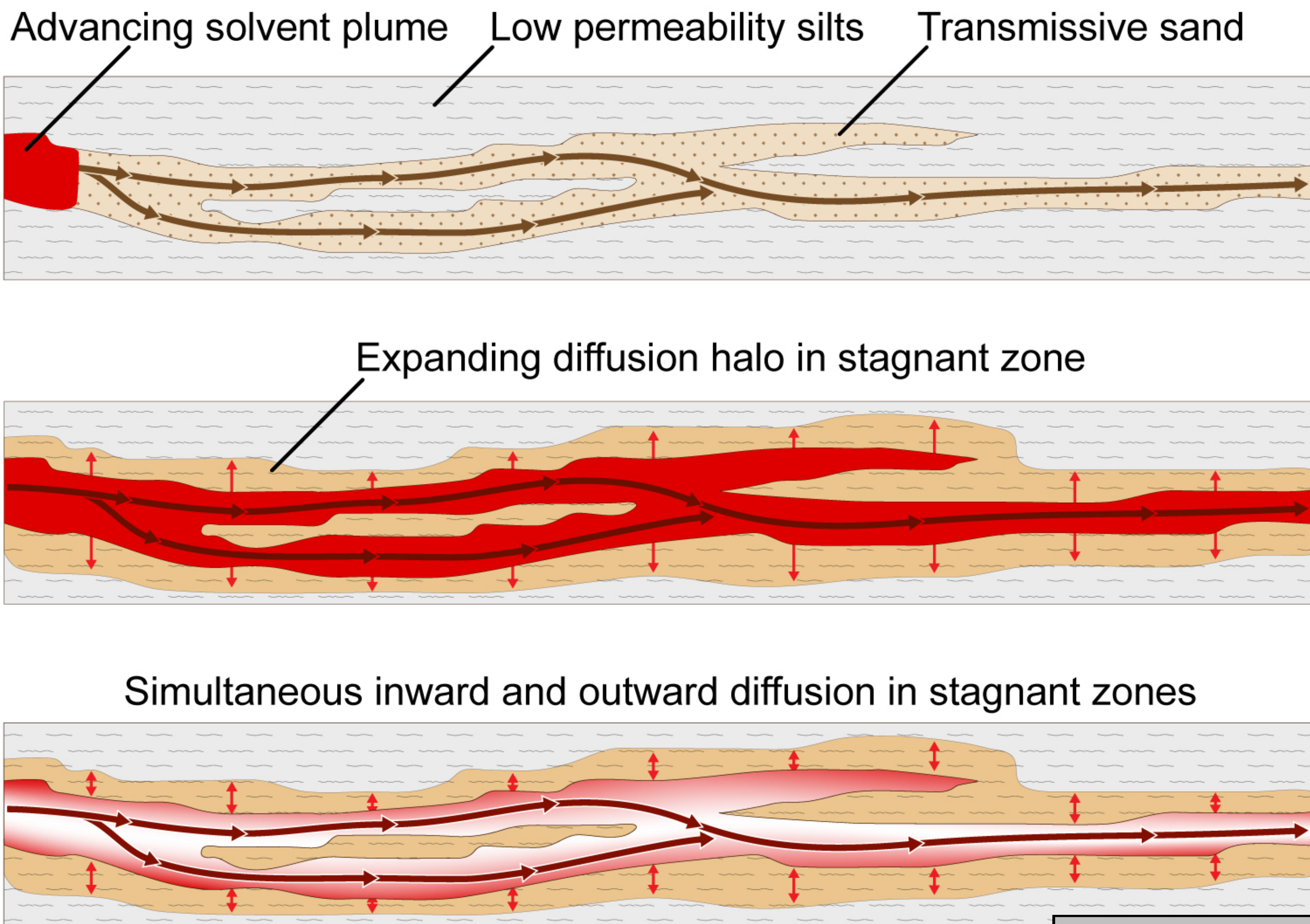
Back Diffusion – The Movie

Lee Ann Doner – (2008) MS CSU

"Sandy aquifers"

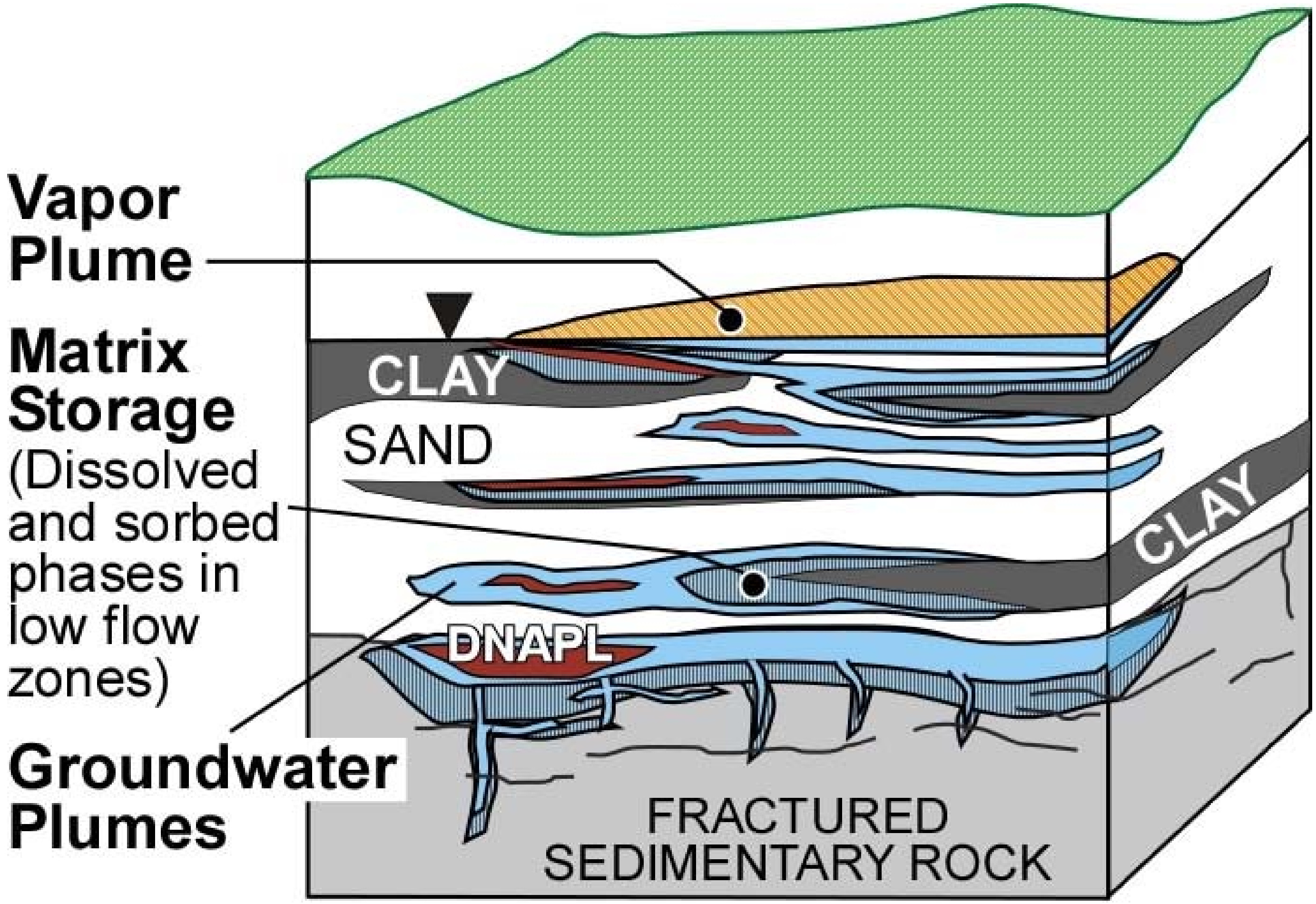
Image from Fred Payne /ARCADIS

New Paradigm



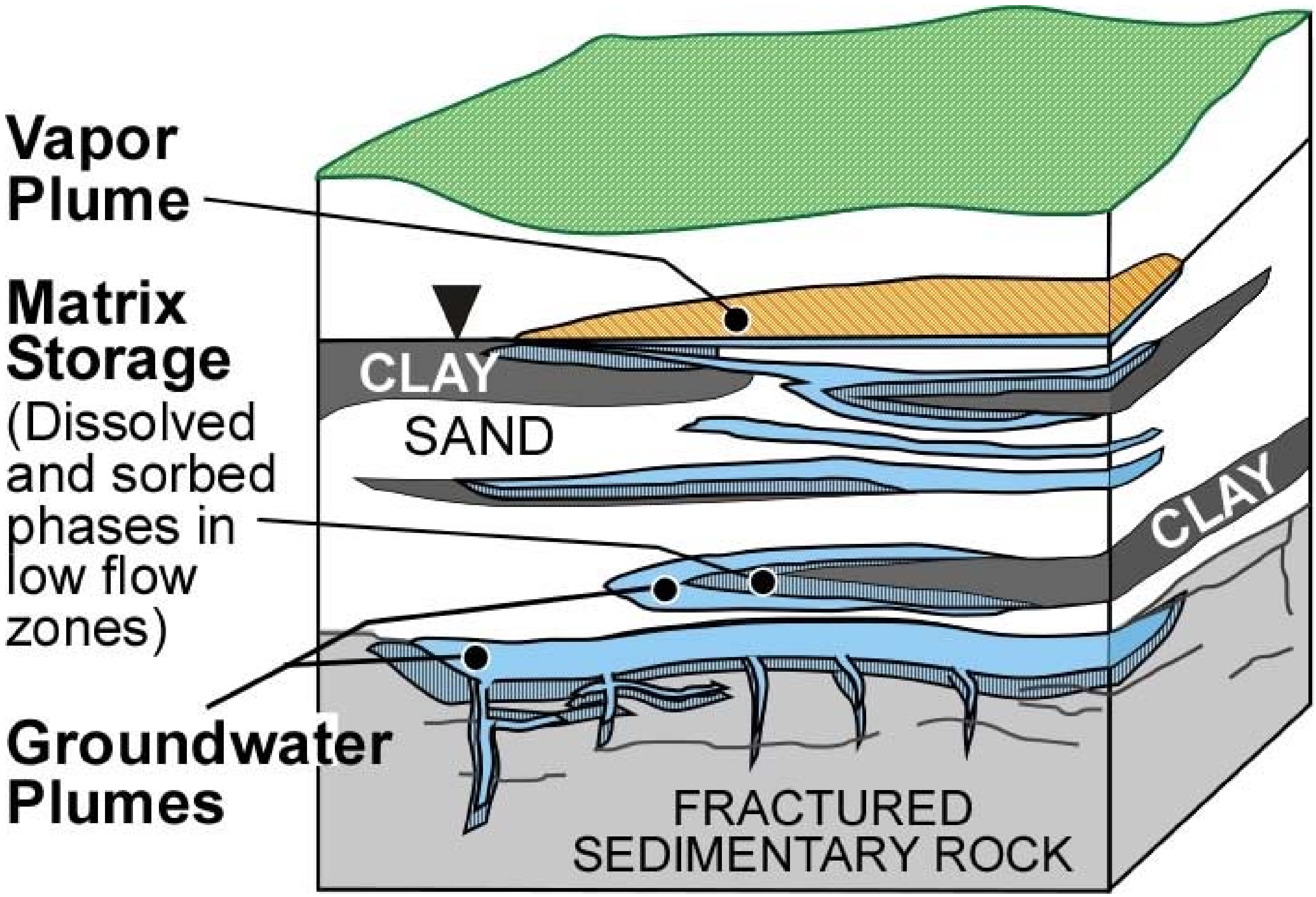
After NRC 2005

Middle Stage



Sale et al., 2008

Late Stage



Sale et al., 2008

The 14 Compartments Model

(a holistic perspective)

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

Sale et al., 2008

With interdependencies (Option 1)

	Source Zone		Plume	
Phase/Zone	Low Permeability	5 Transmissive	6 Transmissive	7 Low Permeability
Vapor				
1 DNAPL 3 2			NA	NA
Aqueous 4				
Sorbed				

With interdependencies (Option 2)

Lattice of 17 potentially relevant fluxes

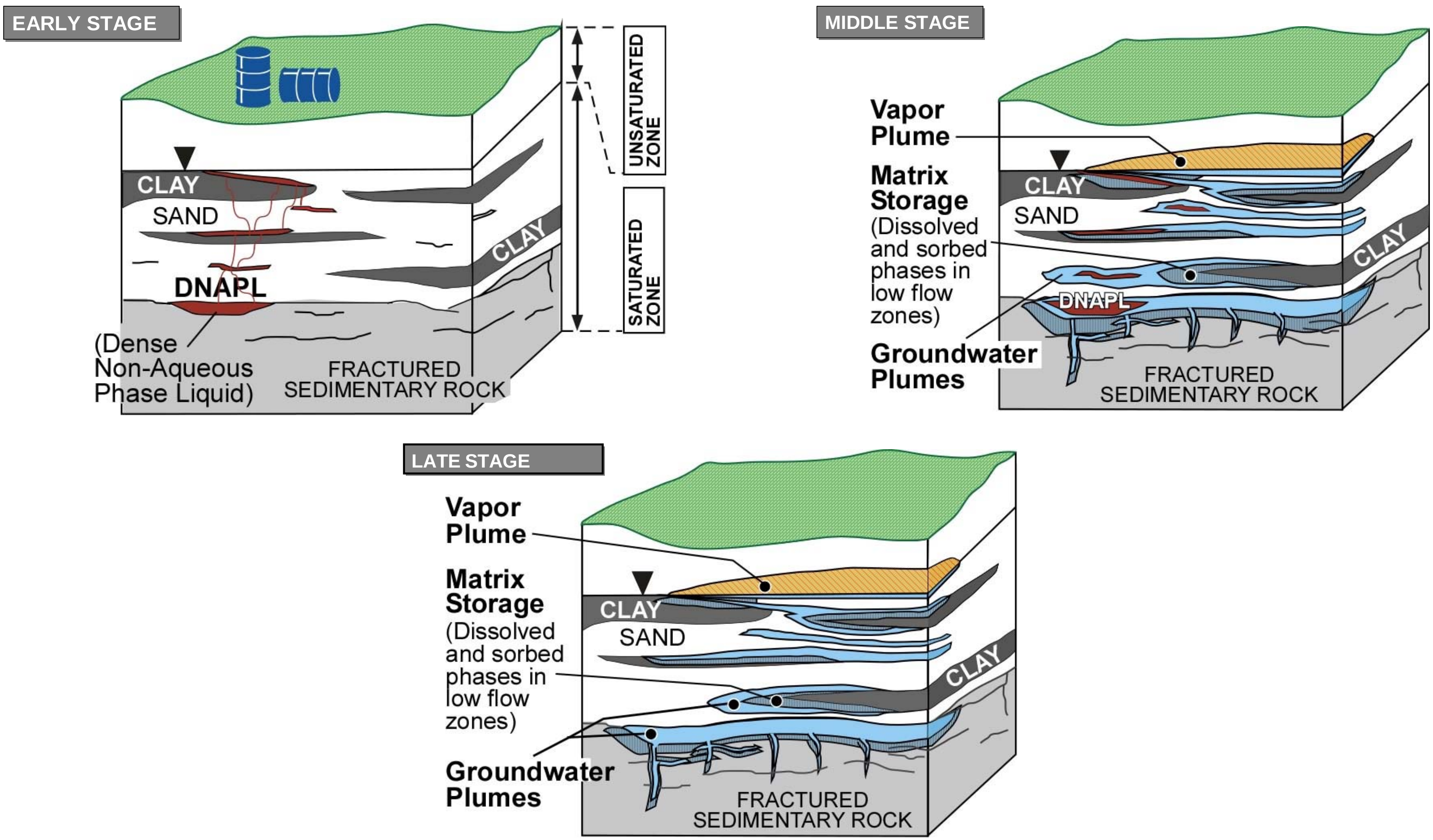
	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

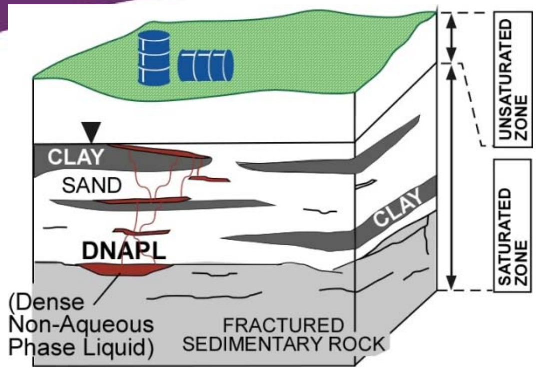
With interdependencies (Option 2)

Lattice of 17 potentially relevant fluxes

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

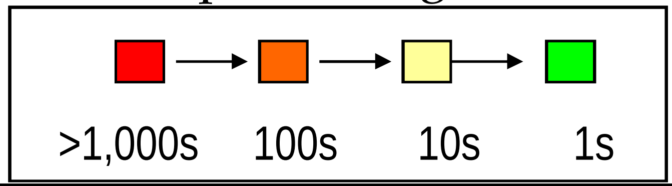
Mapping the evolution of a chlorinated solvent release





Early Stage

Gw. or equivalent gw. conc.



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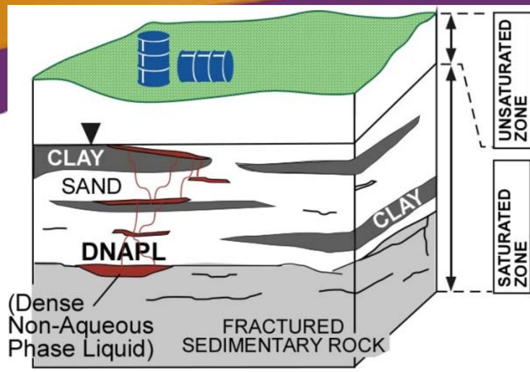
Aqueous				
Sorbed				



Early Stage

>1,000s → 100s → 10s → 1s

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
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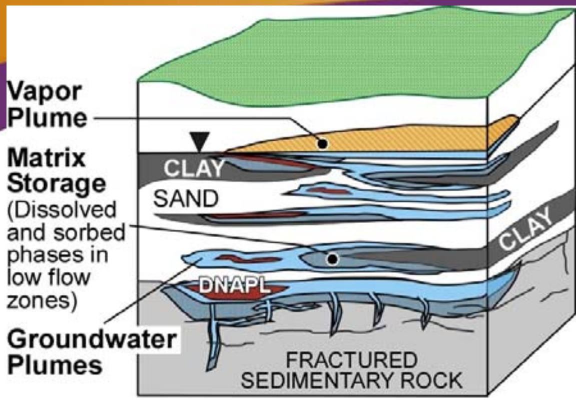
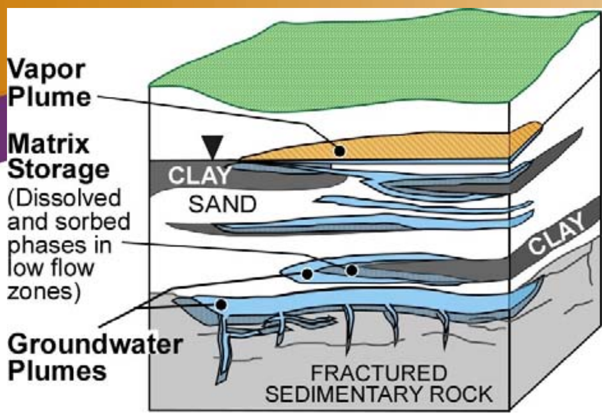


Middle Stage

>1,000s → 100s → 10s → 1s

	Source Zone		Plume	
Phase/Zone	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

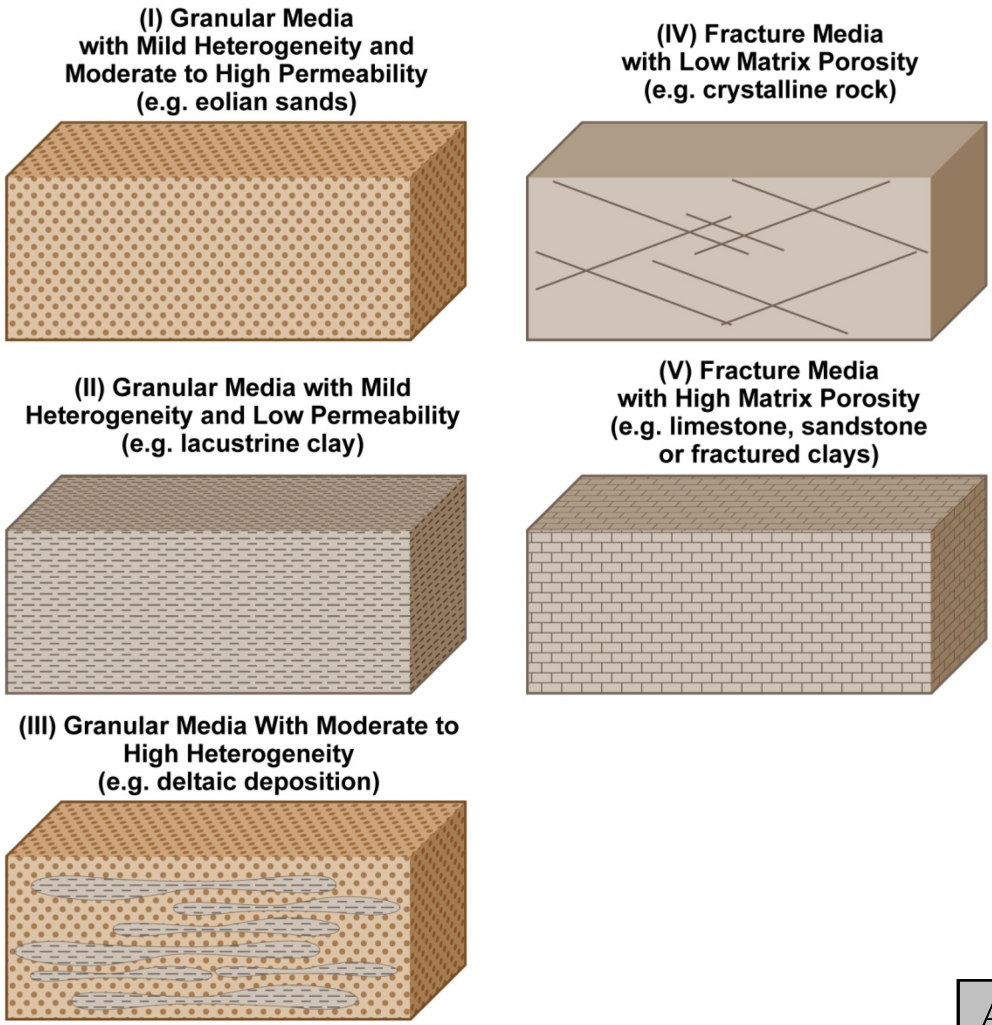


Late Stage

>1,000s → 100s → 10s → 1s

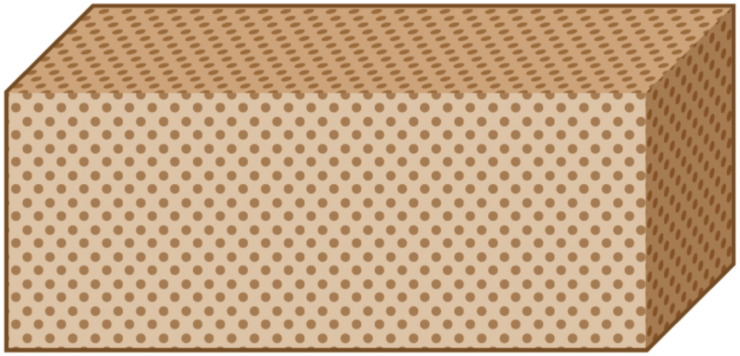
Phase/Zone	Source Zone: Low Permeability	Source Zone: Transmissive	Plume: Transmissive	Plume: Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

Type Setting



After NRC 2005

(I) Granular Media with Mild Heterogeneity and Moderate to High Permeability (e.g. eolian sands)



Great Sand Dunes National Park (Source http://www.nps.gov/grsa)

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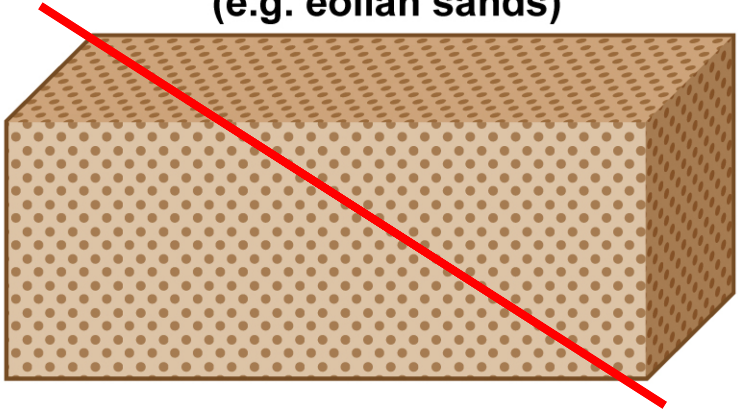
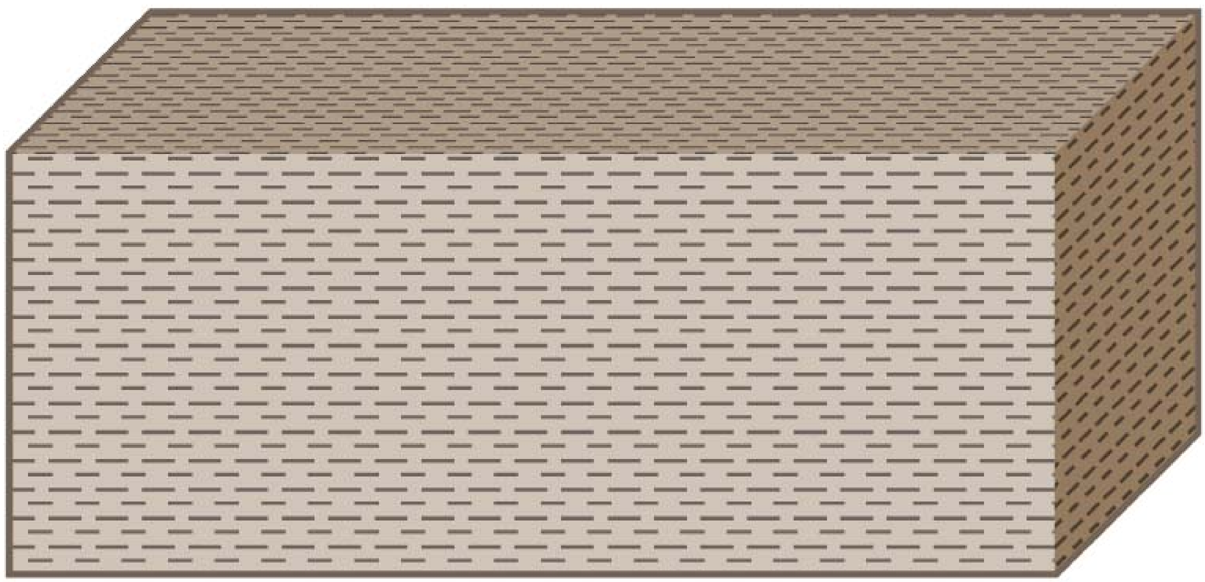


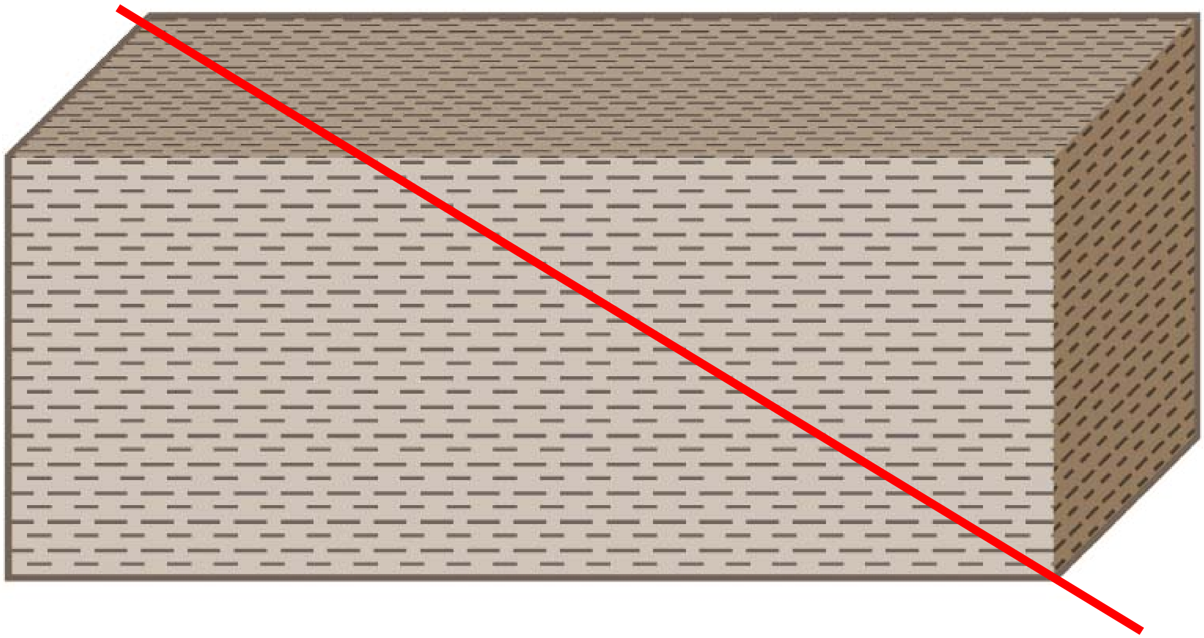
Great Sand Dunes National Park (Source http://www.nps.gov/grsa)

(II) Granular Media with Mild Heterogeneity and Low Permeability (e.g. lacustrine clay)

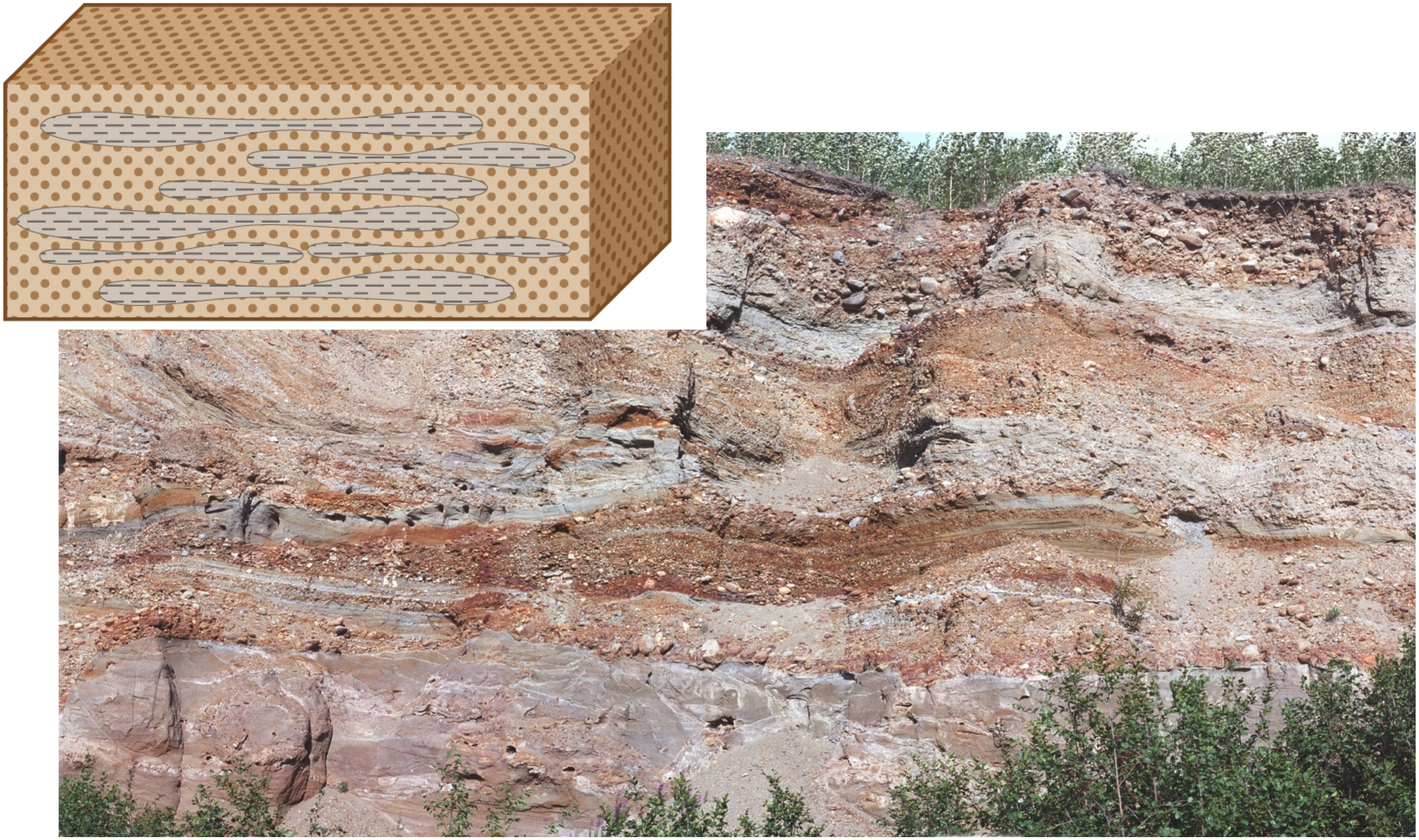


SERDP ESTCP

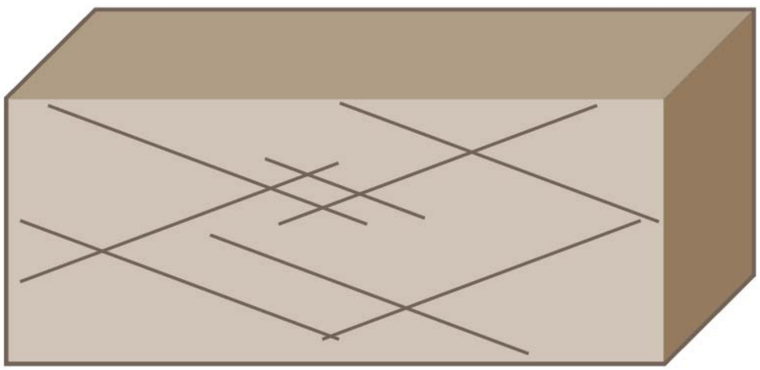
(II) Granular Media with Mild Heterogeneity and Low Permeability (e.g. lacustrine clay)

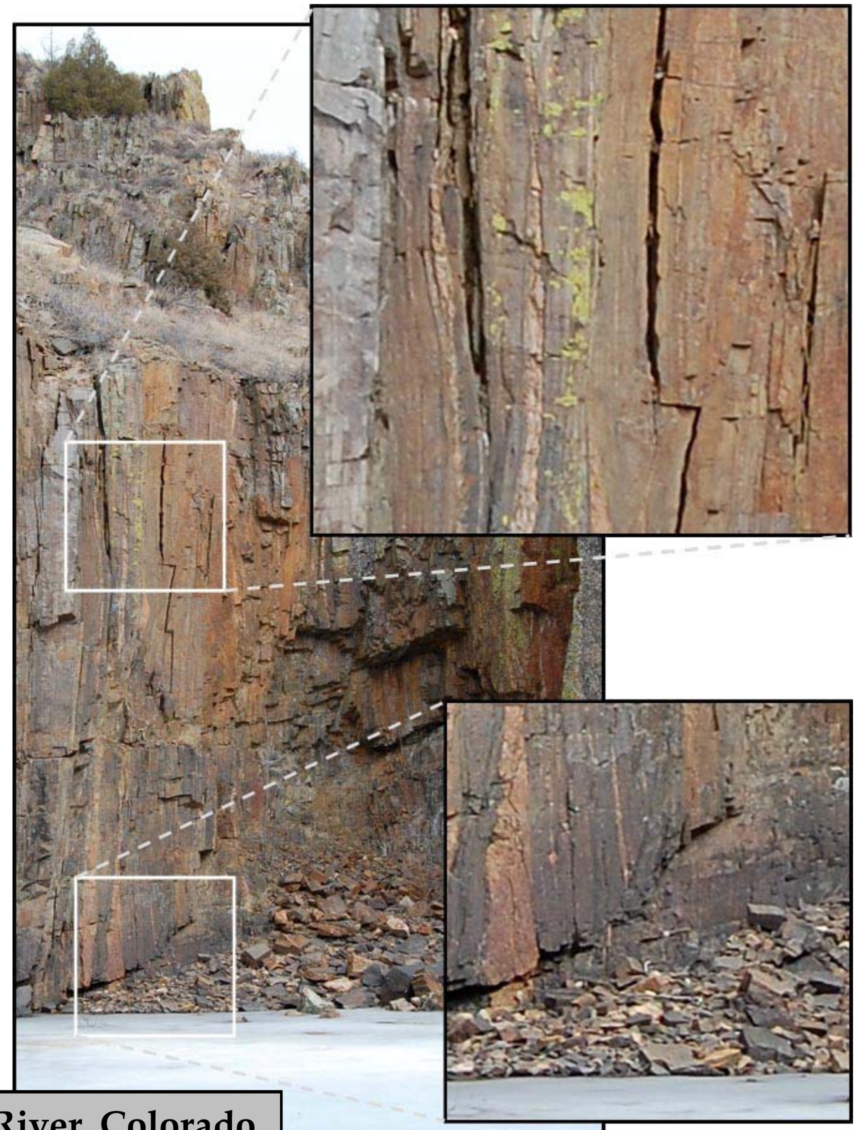


(III) Granular Media With Moderate to High Heterogeneity (e.g. deltaic deposition)



(IV) Fracture Media with Low Matrix Porosity (e.g. crystalline rock)



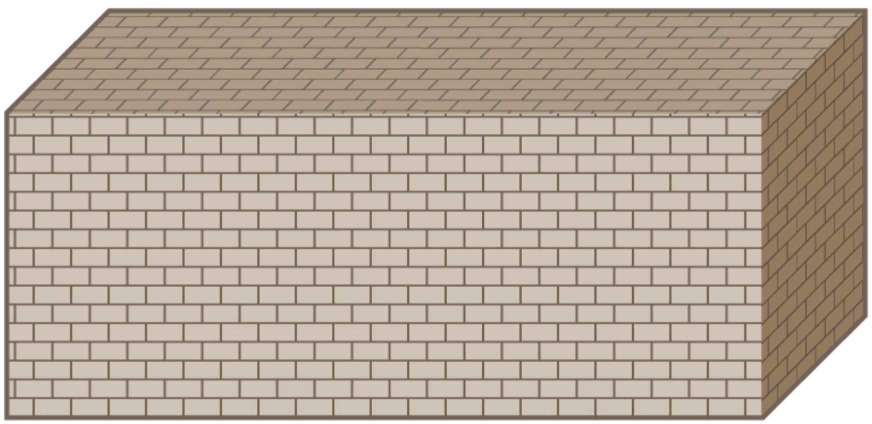


Cache La Poudre River, Colorado

Cache La Poudre River, Colorado

SERDP

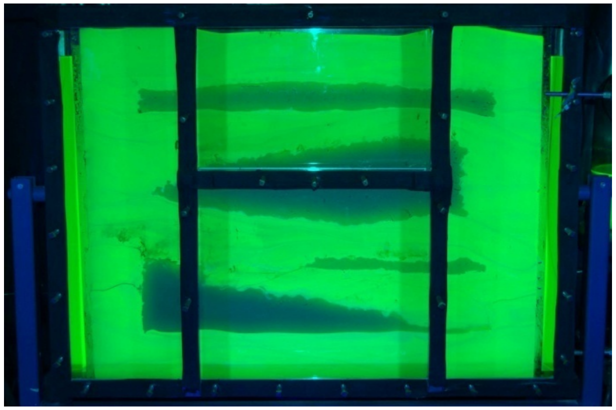
(V) Fracture Media with High Matrix Porosity (e.g. limestone, sandstone or fractured clays)

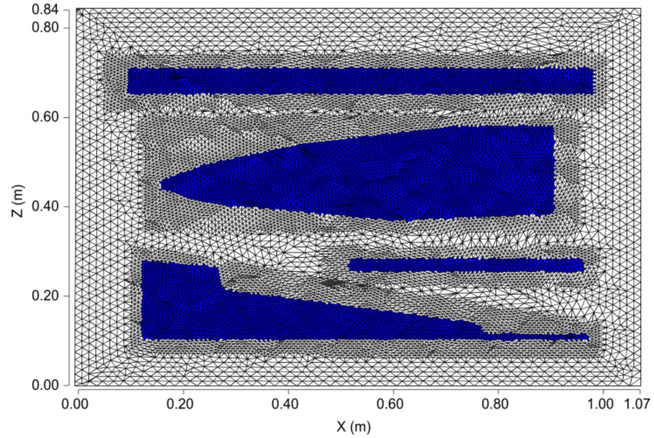


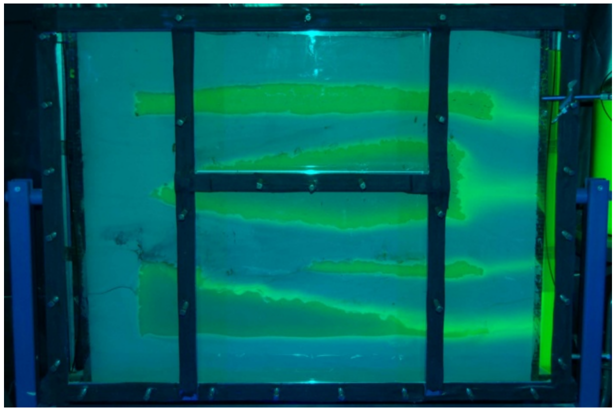
Bedding planes, joints, and vertical fractures in carbonate rock, Southern Ontario, Canada (Courtesy of Dr. Beth Parker)

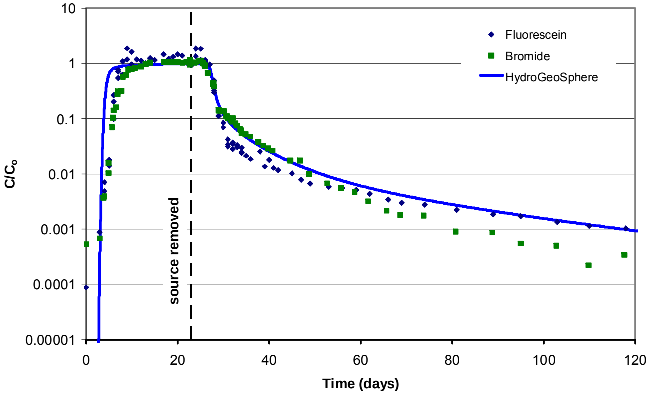
Modeling

With proper grid discretization and time-stepping constraints, standard finite element numerical models can be used to evaluate contaminants in low permeability zones.



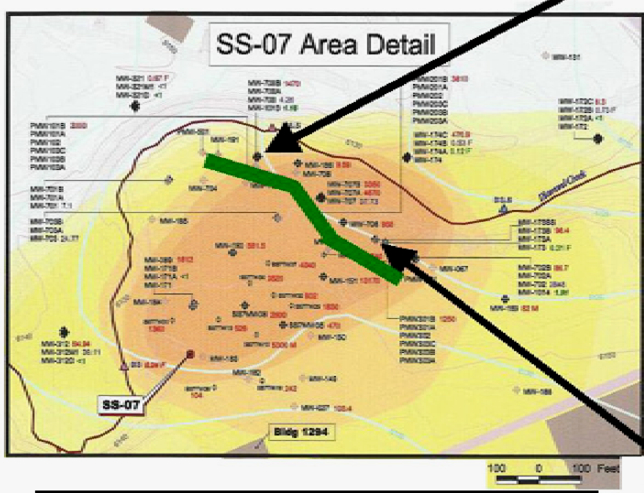




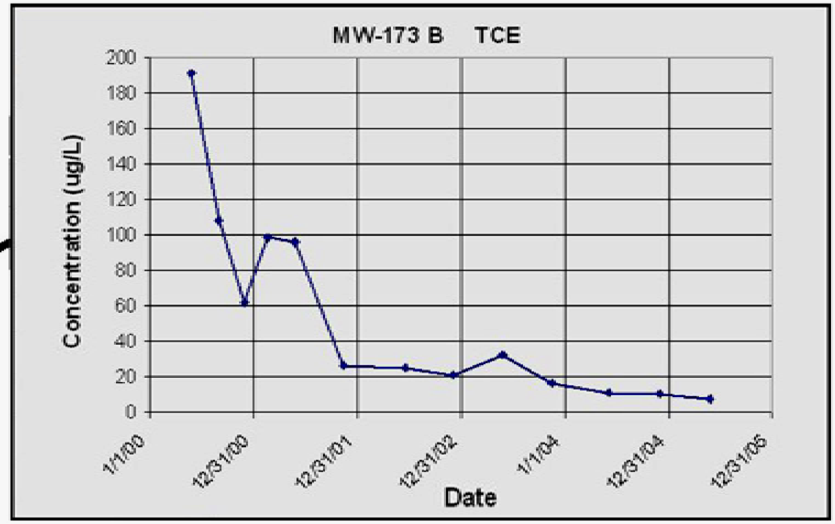


Field site showing impact of low-perm zones

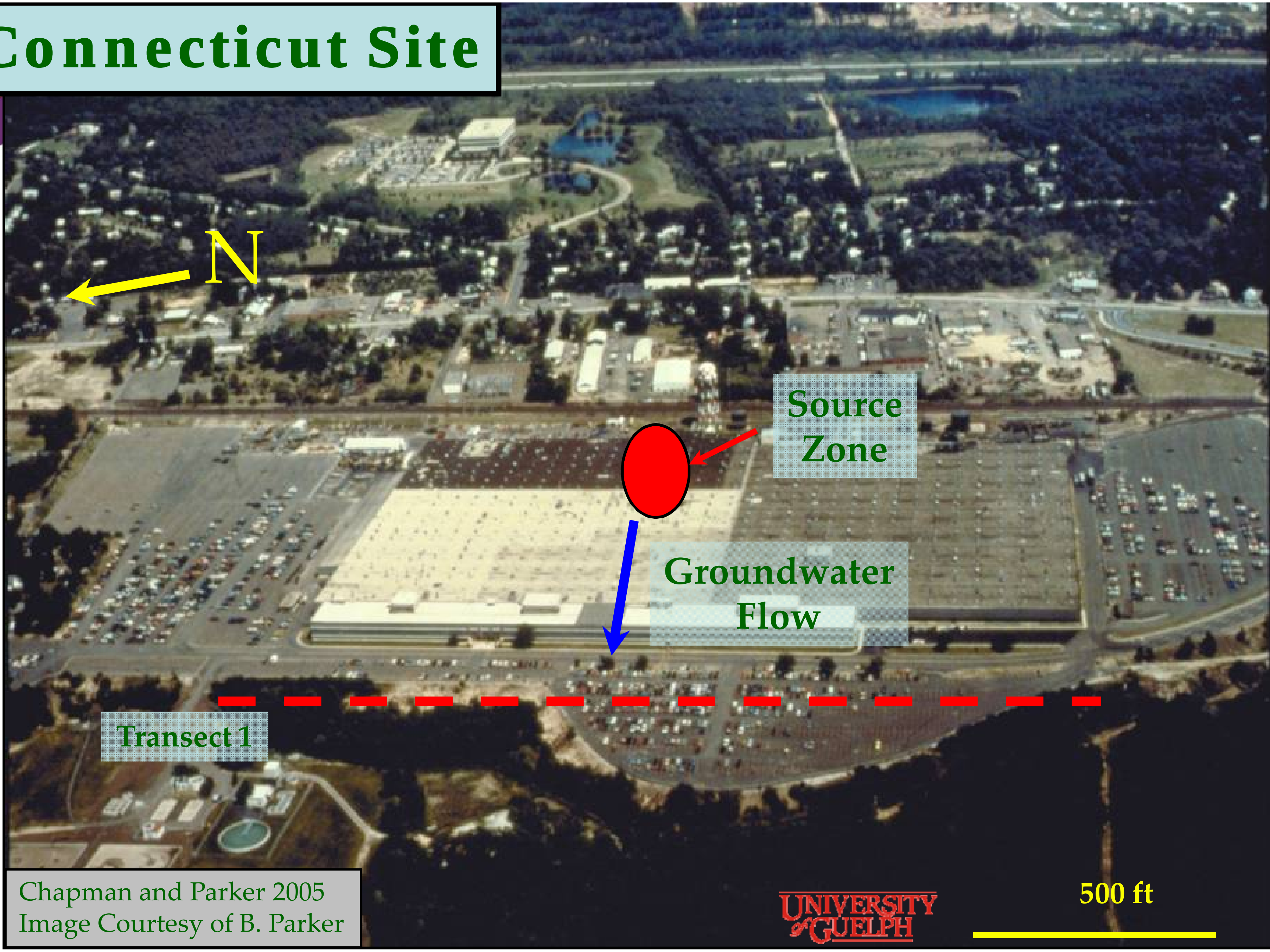
F.E. Warren
Spill Site 7
PRB



Water quality response in a plume downgradient of an iron permeable reactive barrier,
F.E. Warren AFB, Wyoming, AFCEE (2007)

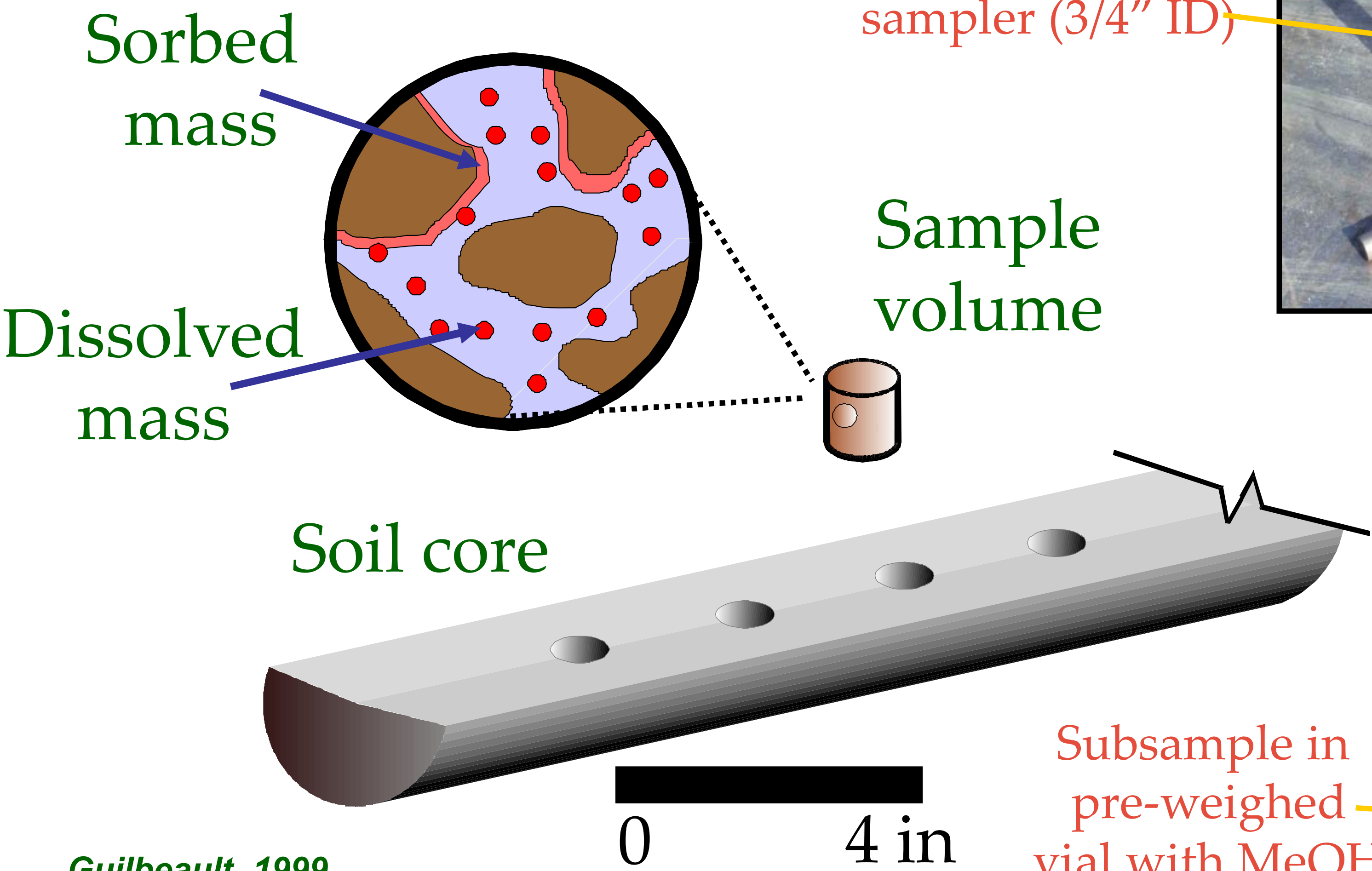


Connecticut Site



Chapman and Parker 2005
Image Courtesy of B. Parker

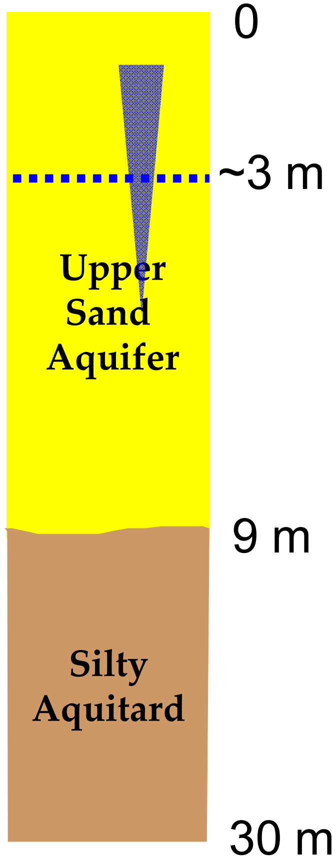
Technical Approach: Soil Core Subsampling (Task 2)



Guilbeault, 1999

Aquifer – Aquitard Contact

Stratigraphic Column



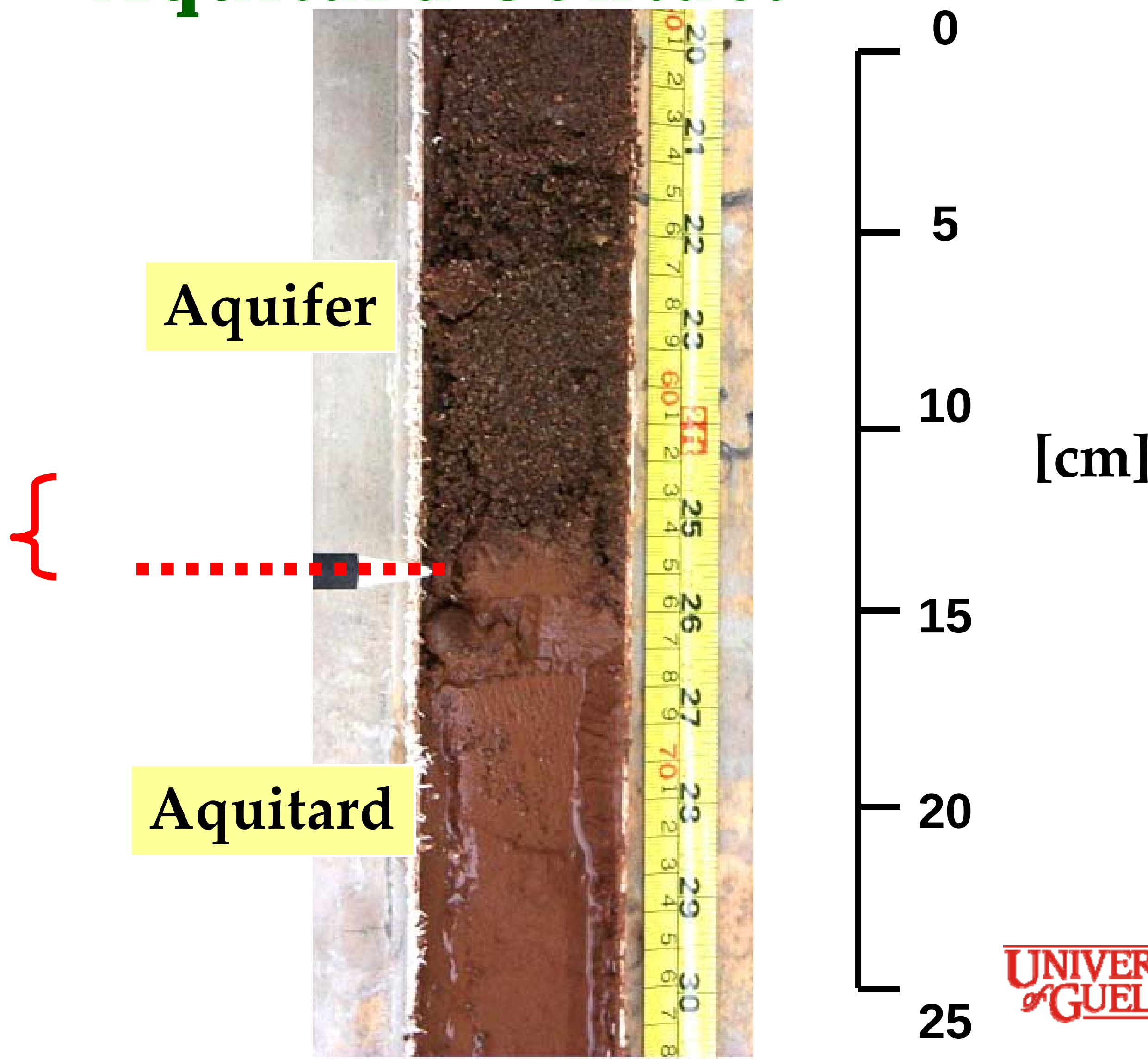
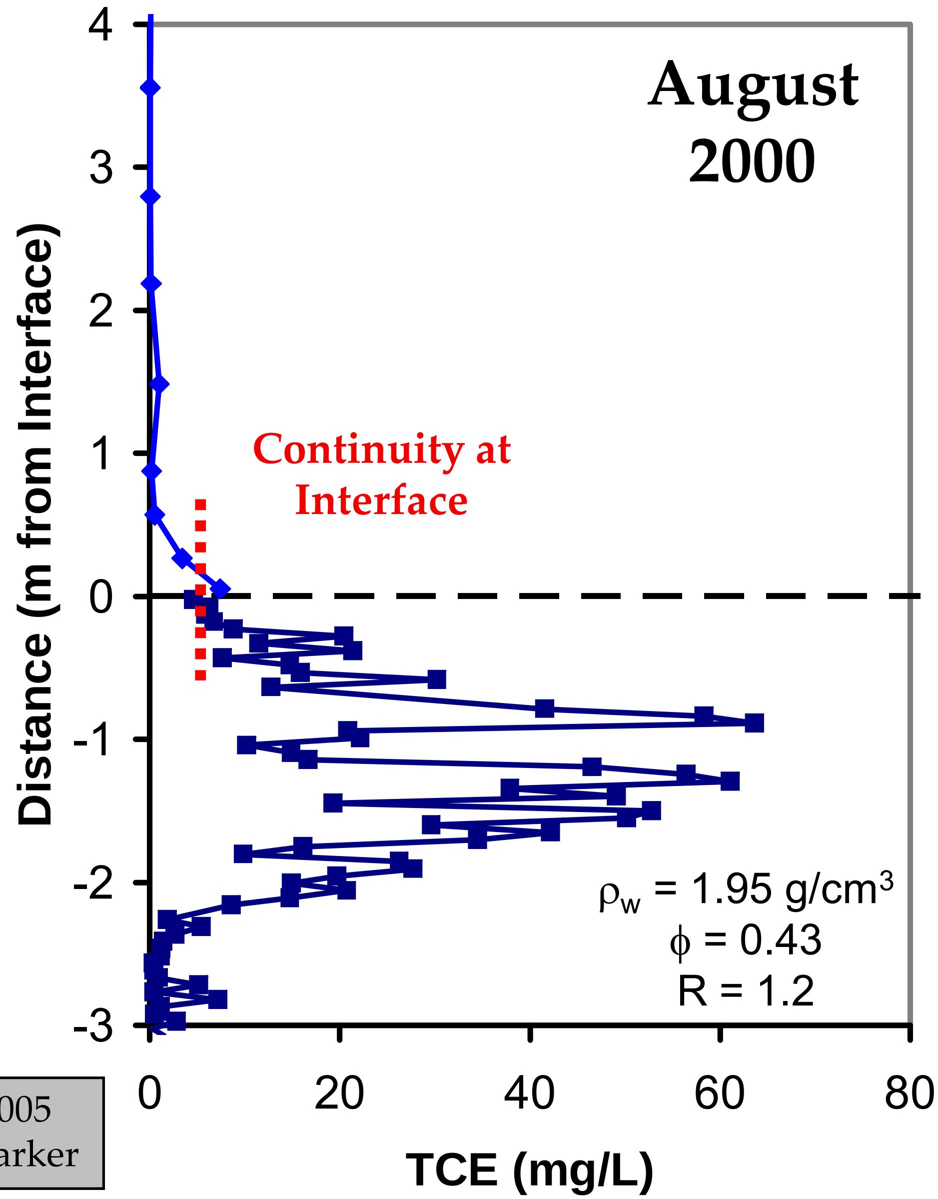
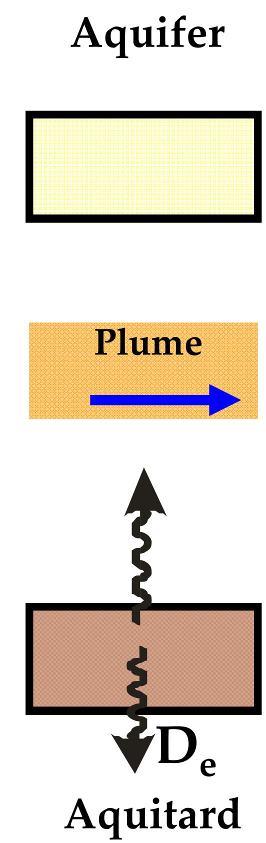


Image Courtesy of B. Parker

High-Resolution Data from Core

Most Mass is in the Aquitard !

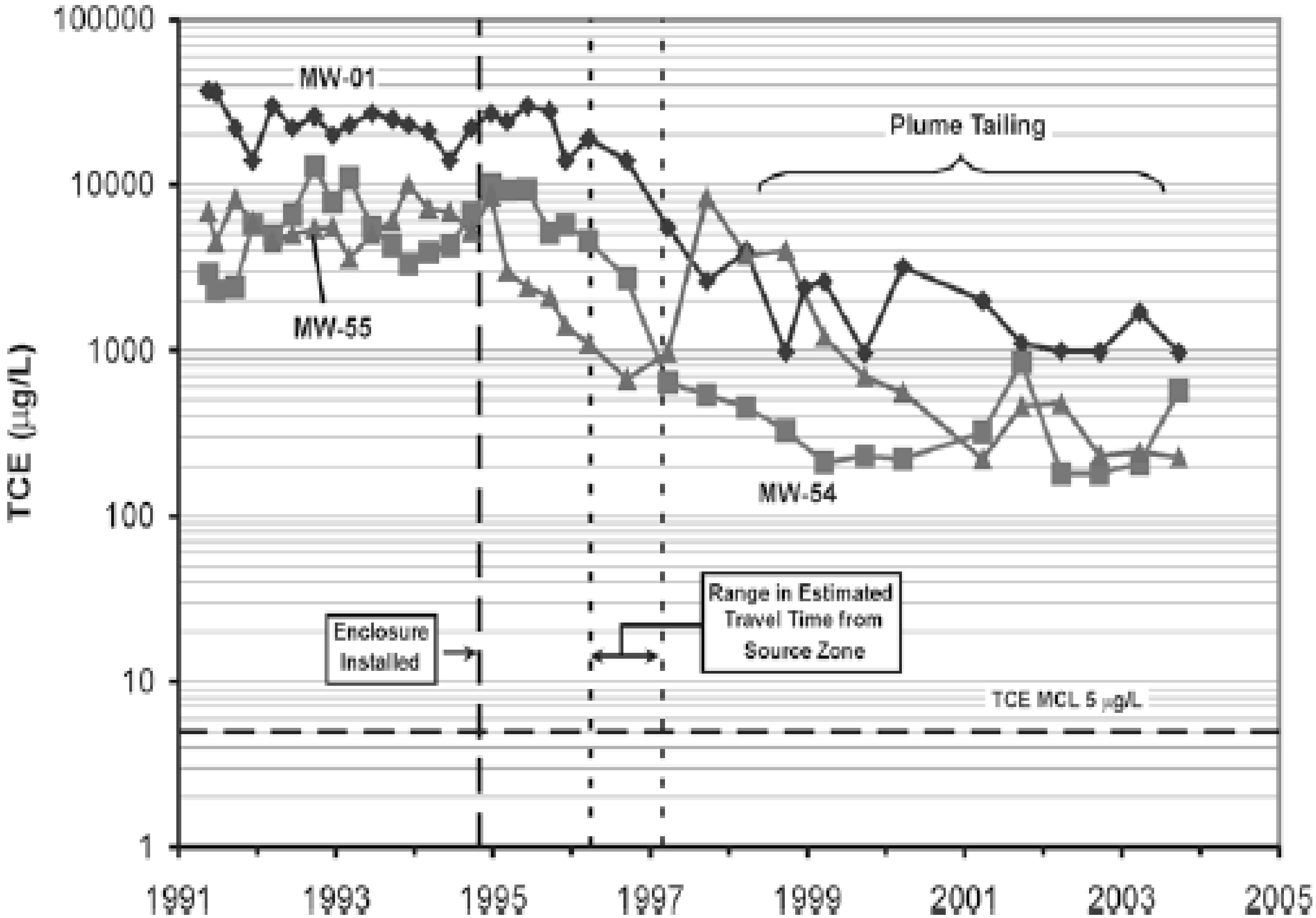




Chapman and Parker 2005
Image Courtesy of B. Parker

UNIVERSITY of GUELPH

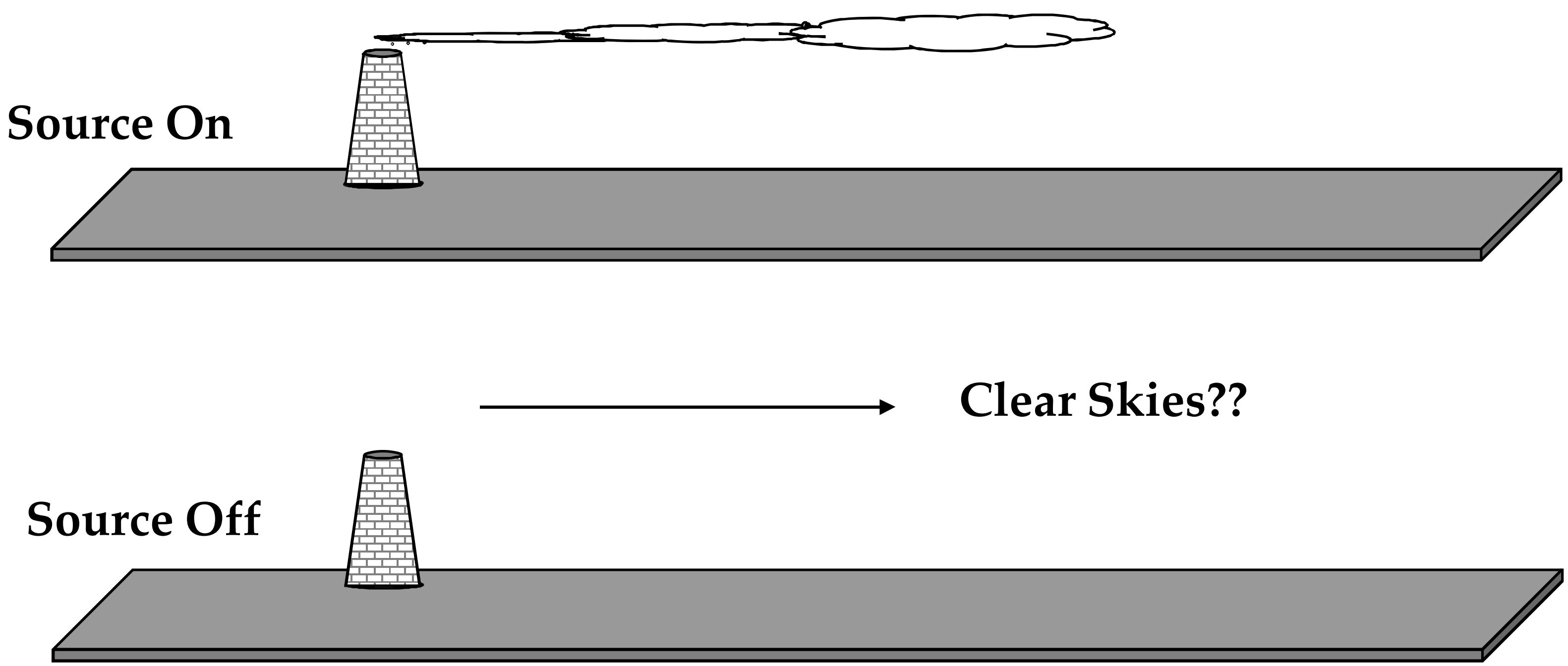
Concentration vs. Time from Monitoring Wells



Source: Chapman and Parker, 2005 Copyright 2005 American Geophysical Union. Reproduced/modified by permission of AGU.

Key Concepts about L&D Plumes

What happens after the "source" is addressed?




© Rolf Hicker

Setting Objectives

Tom Sale, Chuck Newell

University Consortium for Field-Focused Groundwater Contamination Research

University of Guelph, Ontario

May 19-20, 2009

NRC (2005) observations regarding objectives

Failure to explicitly state remedial objectives appears to be a significant barrier …

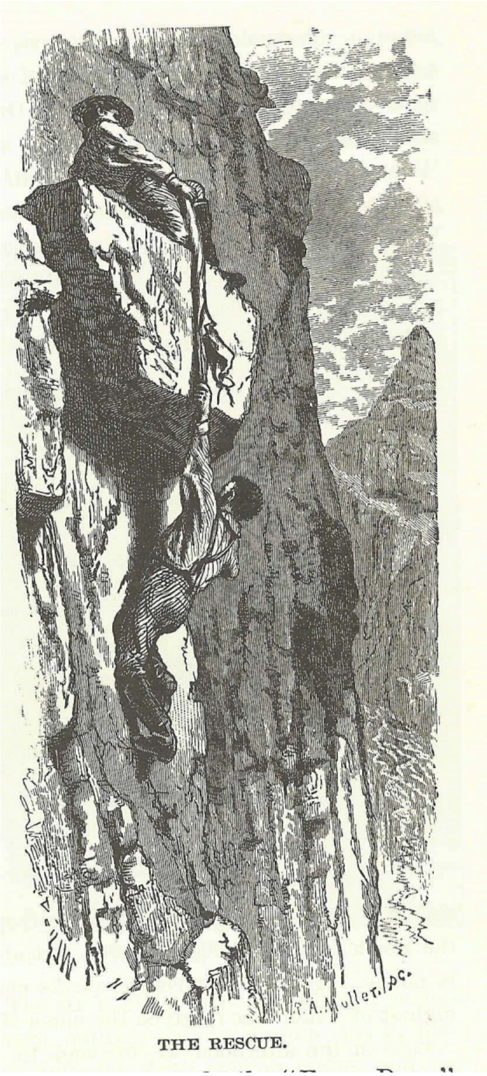
and

Vagueness of objectives for remedial projects can *<u>preclude effective decision making</u>*

Yoggi Berra

- "if you don't know where you are going you might end up someplace else"

- "if you don't know where you are going you might not get there"



John Wesley Powell, Exploration of the Colorado River and its Tributaries

Objectives (NRC 2005)

- Absolute – Broad
- Functional - Specific

Comments on goals

- Set by participating parties
- Reflects the values of the participants
- Site specific
- Different priorities for different participants
- Should not be dictated
- Should be SMART*
  - Specific
  - Measureable
  - <u>Attainable</u>
  - Relevant (or Realistic)
  - Timely

Should be BAV
- Beneficial
- <u>Attainable</u>
- Verifiable

*Peter Drucker "The Practice of Management"

Shopping List - Absolute Objectives

- Protection of human health and the environment
- Conservation of natural resources
- Mitigate adverse community impacts
- Minimize the burden of past practices on future generations

Shopping List – Functional Objectives

- Risk
  - Human Health
  - Ecological receptors
  - Worker
- Extent
  - Limit expansion
  - Reduce footprint
- Reduce Longevity
  - Source
  - Plume
- Regulatory
  - Compliance
- Community
  - Beneficial land use
  - Avoidance of undue disruptions
- Economics
  - Practical costs
  - Limit economic interruptions
  - Sustain property value
- Sustainability
  - Net environmental benefit
  - Passive solutions
  - Effectiveness of combinations
- Resource Conservation
  - Limit future losses
  - Renovation of impacted resources
  - Protect habitat

Absolute Objectives

Functional Objectives

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
Risk				
Prevent active adverse human exposure via groundwater or soil gas				
Prevent active ecological exposure via groundwater or soil gas				
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor				
Extent				
Prevent expansion of source zones and plumes				
Reduce the extent of source zones and plumes				
Longevity				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.				
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.				
Regulatory				
Comply with local, state, and federal regulations				
Community				
Address adverse (non-health) impacts to communities				
Land use				
Restore beneficial use of impacted lands				
Economic				
Select actions that have a practical near terms capital costs and minimal life cycle cost				
Avoid undue interruptions to communities, government, and industry activities				
Redress adverse impacts to property values				
Sustainability				
Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
Enhance the effectiveness of complementary technologies				
Resource Conservation				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

The Perfect Remedy

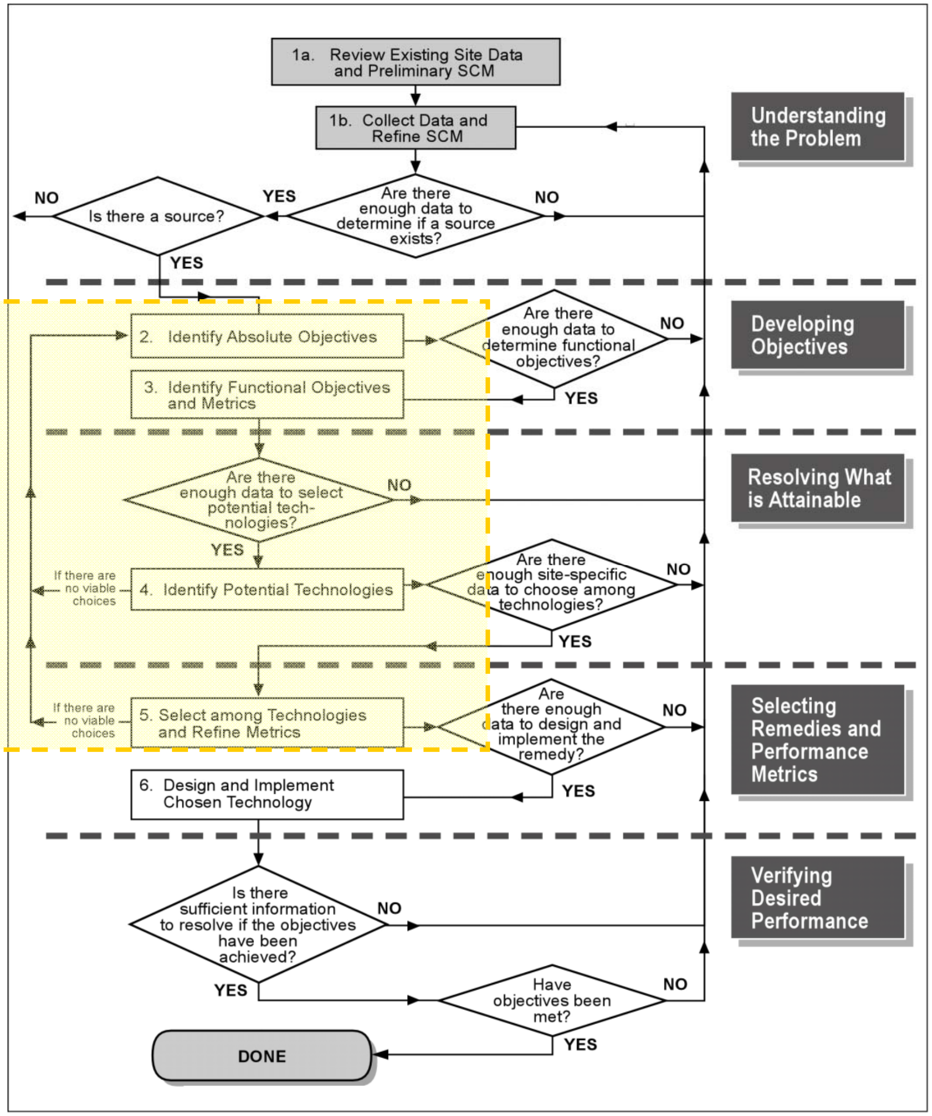
Absolute Objectives

Functional Objectives

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
Risk				
Prevent active adverse human exposure via groundwater or soil gas				
Prevent active ecological exposure via groundwater or soil gas				
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor				
Extent				
Prevent expansion of source zones and plumes				
Reduce the extent of source zones and plumes				
Longevity				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.				
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.				
Regulatory				
Comply with local, state, and federal regulations				
Community				
Address adverse (non-health) impacts to communities				
Land use				
Restore beneficial use of impacted lands				
Economic				
Select actions that have a practical near terms capital costs and minimal life cycle cost				
Avoid undue interruptions to communities, government, and industry activities				
Redress adverse impacts to property values				
Sustainability				
Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
Enhance the effectiveness of complementary technologies				
Resource Conservation				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

Iterative Nature of Setting Goals

- Desired outcome
- Remedy Selection
- Prediction of outcome
- Comparison to goals
- …



NRC 2005

Selecting technologies

What technologies do

- Treatment
  - Flux reduction
  - Longevity reduction
- Containment
  - Flux reduction

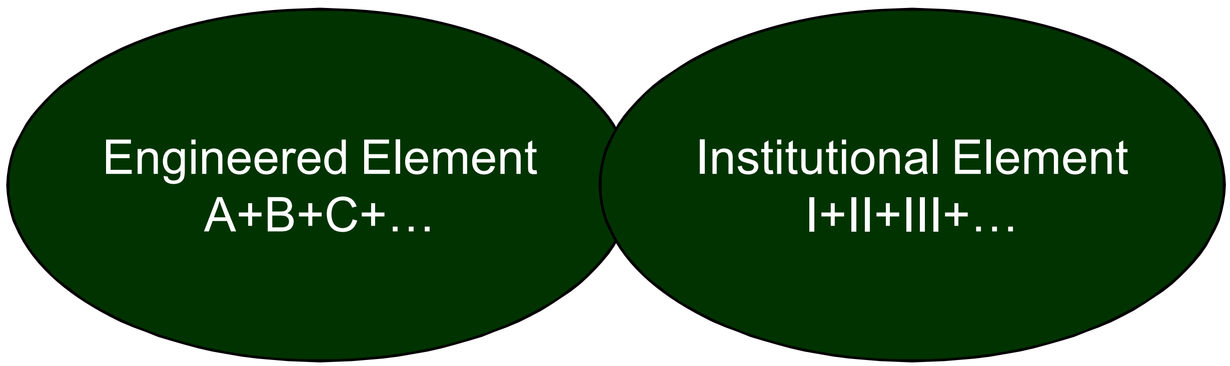
General classes of proven <u>treatment</u> technologies addressed include

- Physical Processes
- In Situ Chemical Oxidation
- In Situ Chemical Reduction
- In Situ Biological Reduction
- Thermal

General classes of proven <u>containment</u> technologies addressed include

- Hydraulic Containment (Pump and Treat)
- Hydraulic barriers
- Coupled Hydraulic-Physical Containment
- In Situ Stabilization
- Permeable Reactive Barriers

Combined Remedies



OoM Rules of Thumb

- Well implemented in-situ remediation remedies are likely to reduce source zone groundwater concentrations by **about *one order-of-magnitude* (90% reduction)** from pre-treatment levels.

- **One order-of-magnitude source reduction…**
  - **gives one order-of-magnitude improvement downgradient water quality.**
- **But with fast groundwater flow, low mass storage, and/or active attenuation…**
  - **potentially gives 2-3 orders-of-magnitude improvement downgradient over several years**

Mapping technology performance using the 14 compartment model

Pump & Treat

<table>
<tr><th rowspan="2">Phase / Zone</th><th colspan="2">Source Zone</th><th colspan="2">Plume</th></tr>
<tr><th>Low Permeability</th><th>Transmissive</th><th>Transmissive</th><th>Low Permeability</th></tr>
<tr><td>Vapor</td><td colspan="4">Extraction of contaminated groundwater from transmissive zones is likely to have little effect on vapor in the vadose zone.</td></tr>
<tr><td>DNAPL</td><td rowspan="3">Depletion of aqueous phase from transmissive zones will cause slow release from low permeability zones</td><td>DNAPL has the potential to be a long term source of aqueous phase</td><td colspan="2">Not Applicable</td></tr>
<tr><td>Aqueous</td><td>Pumping groundwater from the source zone will cause direct depletion of aqueous phase in transmissive zones</td><td>Pumping groundwater from the source zone will drive direct depletion of aqueous phase in transmissive zones</td><td rowspan="2">Depletion of aqueous phase from transmissive zones will drive slow release from low permeability zones in plumes</td></tr>
<tr><td>Sorbed</td><td colspan="2">Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process</td></tr>
</table>

How Does PUMP AND TREAT* Affect Contaminants in the 14 Different Compartments?

* (when used for treatment, not containment)

Key: Technology has this effect on contaminants in this compartment:

- *Direct depletion*
- *Depletion but as a secondary effect*
- *Limited secondary effect*
- *Largely unaffected*

Orders of Magnitude (OoM)

DEGREE OF CONTAMINATION	
Degree of Contamination	Level described by equivalent concentrations in water
3 = Very High	1 – 10s (plus) mg/L in water
2 = High	100 -1000 ug/L in water
1 = Moderate	10-100 ug/L
0 = Low	1-10 ug/L

Anticipated Performance	
Description	Approximate Removal
3 = Direct	> 90%
2 = Secondary	90-10 %
1 = Limited	< 10% -1%
0 = Largely Unaffected	<1%

Distribution of chlorinated solvents in a late stage Type IV setting

(Fractured rock with low matrix porosity)

	Source Zone		Plume	
Zone/Phase	Low Permeability	Transmissive	Transmissive	Low Permeability
Vapor	0	0	0	0
DNAPL	0	0		
Aquesous	0	1	1	0
Sorbed	0	1	1	0

Distribution of chlorinated solvents in a late stage
Type 4 setting (Fractured Rock with Low Matrix Porosity)

Pump and treat in a late stage Type IV setting

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	0	0	0	0	0	0	0
DNAPL	1	0	1	0				
Aqueous	1	0	3	1	3	1	1	0
Sorbed	1	0	2	1	2	1	1	0

Maxium	**12**	**Actual**	**10**	**Score**	**83**

Screening pump and treat in a middle stage Type III setting.

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aqueous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

Maximum	**81**	**Actual**	**36**	**Score**	**44**

Outcome from pump and treat

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aquesous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

Maxium	**81**	**Actual**	**36**	**Score**	**44**

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	0	2	0	2	0	1	0	1
DNAPL	1	2	1	3				
Aquesous	1	2	3	3	3	2	1	1
Sorbed	1	2	2	3	2	2	1	1

Source Excavation

	Source Zone		Plume	
Phase / Zone	**Low Permeability**	**Transmissive**	**Transmissive**	**Low Permeability**
Vapor	Assuming that the entire source zones is removed, and properly backfilled, no contamination should remain in the source zones		May reduce vadose zone vapor concentrations	
DNAPL			Not Applicable	
Aqueous			Removal of the upgradient source should yield 1 to 3 order of magnitude improvements in downgradient water quality	Depletion of contamination in the transmissive zones results in slow release of aqueous and sorbed phases in low permeability zones
Sorbed			Depletion of the aqueous phase in transmissive zones will drive release of sorbed compounds. Note release of sorbed phase can be a slow process.	

Source excavation as a function of age

Source excavation in an early stage Type 3 setting.

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	3	1	3	2	1	0	1	0
DNAPL	3	1	3	3				
Aqueous	3	1	3	3	2	1	1	0
Sorbed	3	1	3	3	2	0	1	0

Maxium	48	Actual	47	Score	98

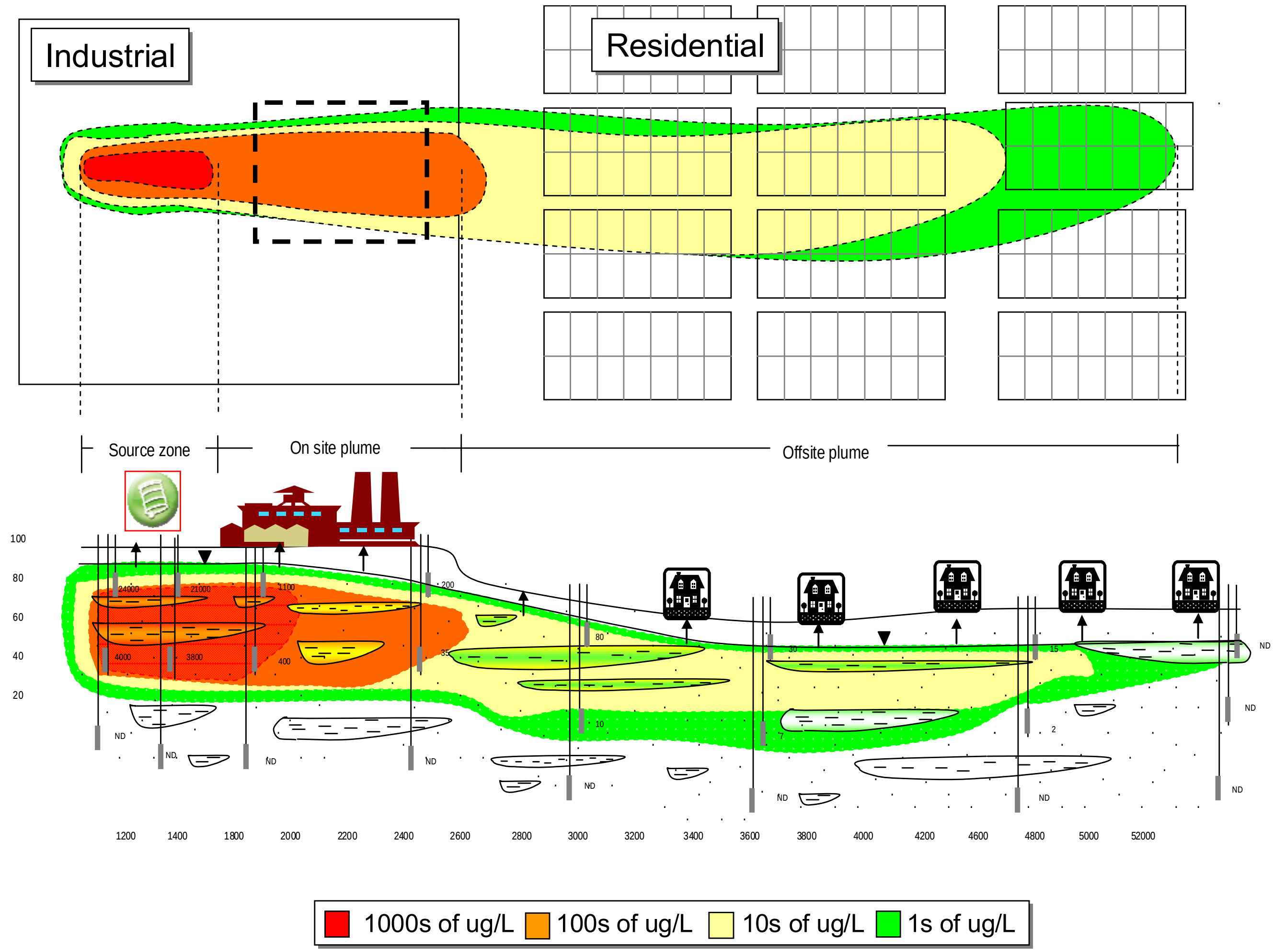
Source excavation in a late stage Type 3 setting.

	Source Zone				Plume			
Zone/Phase	Low Permeability		Transmissive		Transmissive		Low Permeability	
Vapor	3	1	3	1	1	1	1	1
DNAPL	3	0	3	0				
Aquesous	3	2	3	1	2	1	1	2
Sorbed	3	2	3	1	2	1	1	2

Maximum	48	Actual	34	Score	71

Packaging Remedies

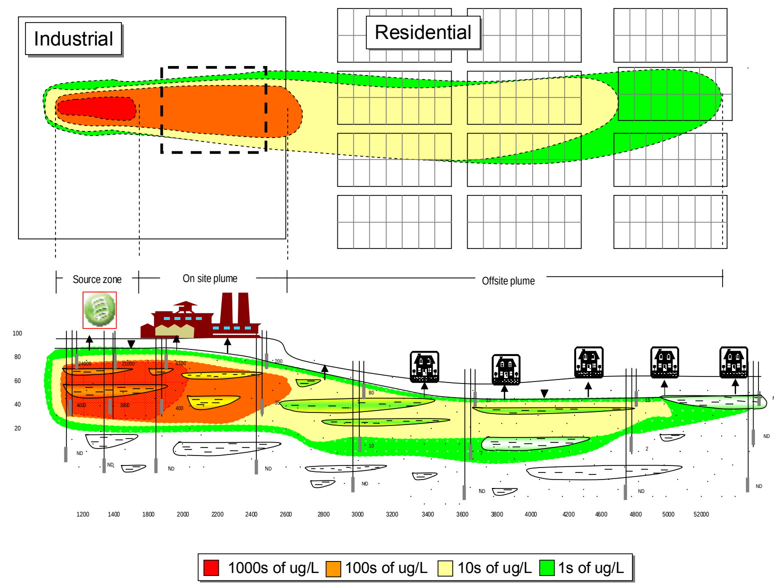
Example N0. 1



Industrial
Residential
Source zone
On site plume
Offsite plume
1000s of ug/L
100s of ug/L
10s of ug/L
1s of ug/L

Site attributes

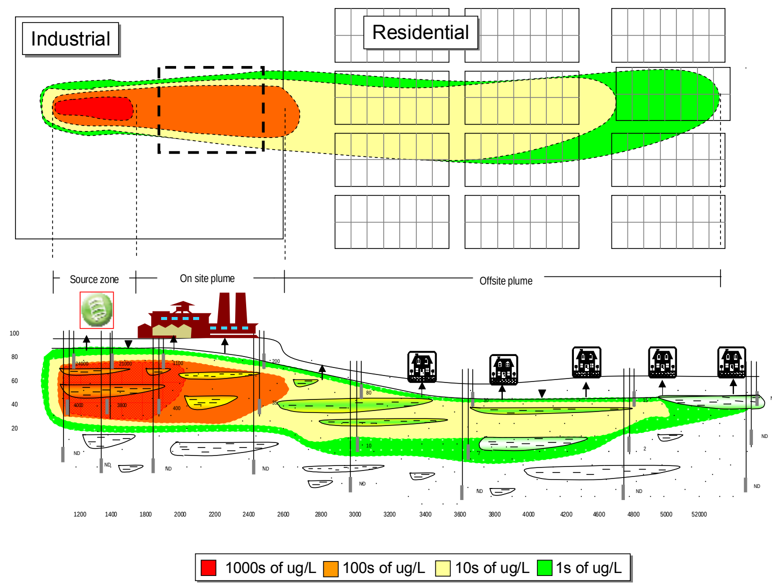
- 30 year old release of chlorinated solvent
- ~ 1 mile plume in a sandy aquifer
- 1000s of ug/L in the source area to 1s of ug/L at the end of the plume



- No DNAPL observed in the source zone
- Stable plume with active degradation
- Lower permeability media (clays layers) are accumulating contaminant via inward diffusion
- Indoor air is a concern in the residential area

Drivers

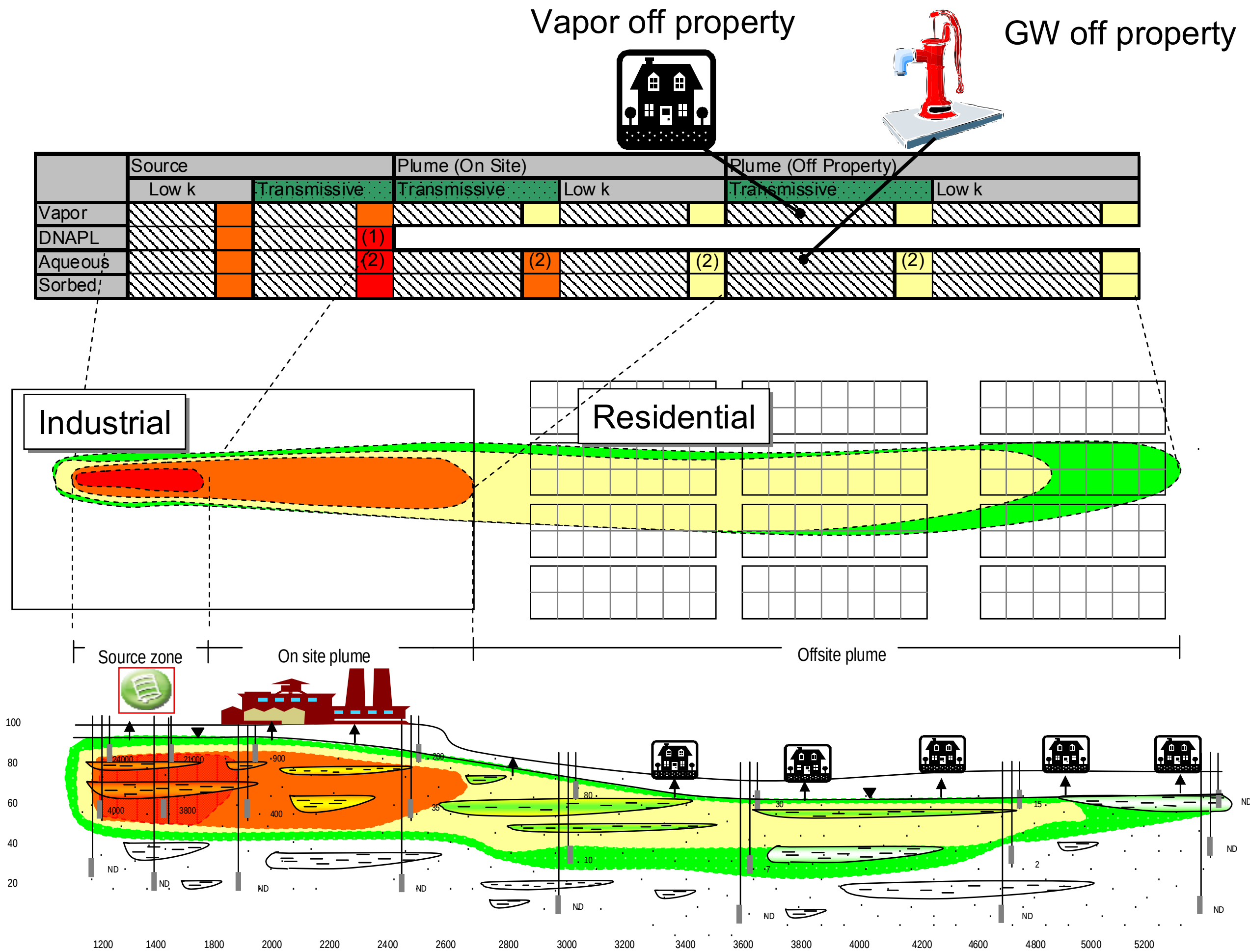
- Home owners are concerned about health effects, property values, and disruptions in the neighborhood.
- Regionally, the community is committed to a clean environment while wanting to preserve jobs.



- Facility is committed to immediately addressing exposure pathways and meeting all other obligations with constraints of –
  - ♦ a preference for actions with consequential benefits
  - ♦ economically feasibility
- Regulators support the interests of the community, provide technical support, and pursue compliance.

Before Treatment

- Setting
  - Middle stage
  - Type II
  - Cont. in low k zones
- With potential exposure via
  - Vapor
  - Groundwater
  - Onsite worker



Consensus goals

Not Applicable

To be defined

	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
Risk				
Prevent active adverse human exposure via groundwater or soil gas				
Prevent active ecological exposure via groundwater or soil gas				
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor				
Extent				
Prevent expansion of source zones and plumes				
Reduce the extent of source zones and plumes				
Longevity				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.				
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.				
Regulatory				
Comply with local, state, and federal regulations				
Community				
Address adverse (non-health) impacts to communities				
Land use				
Restore beneficial use of impacted lands				
Economic				
Select actions that have a practical near terms capital costs and minimal life cycle cost				
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Select measures that have a net positive environmental benefit				
Progress to a state in which passive remedies will be sufficient to address residual impacts				
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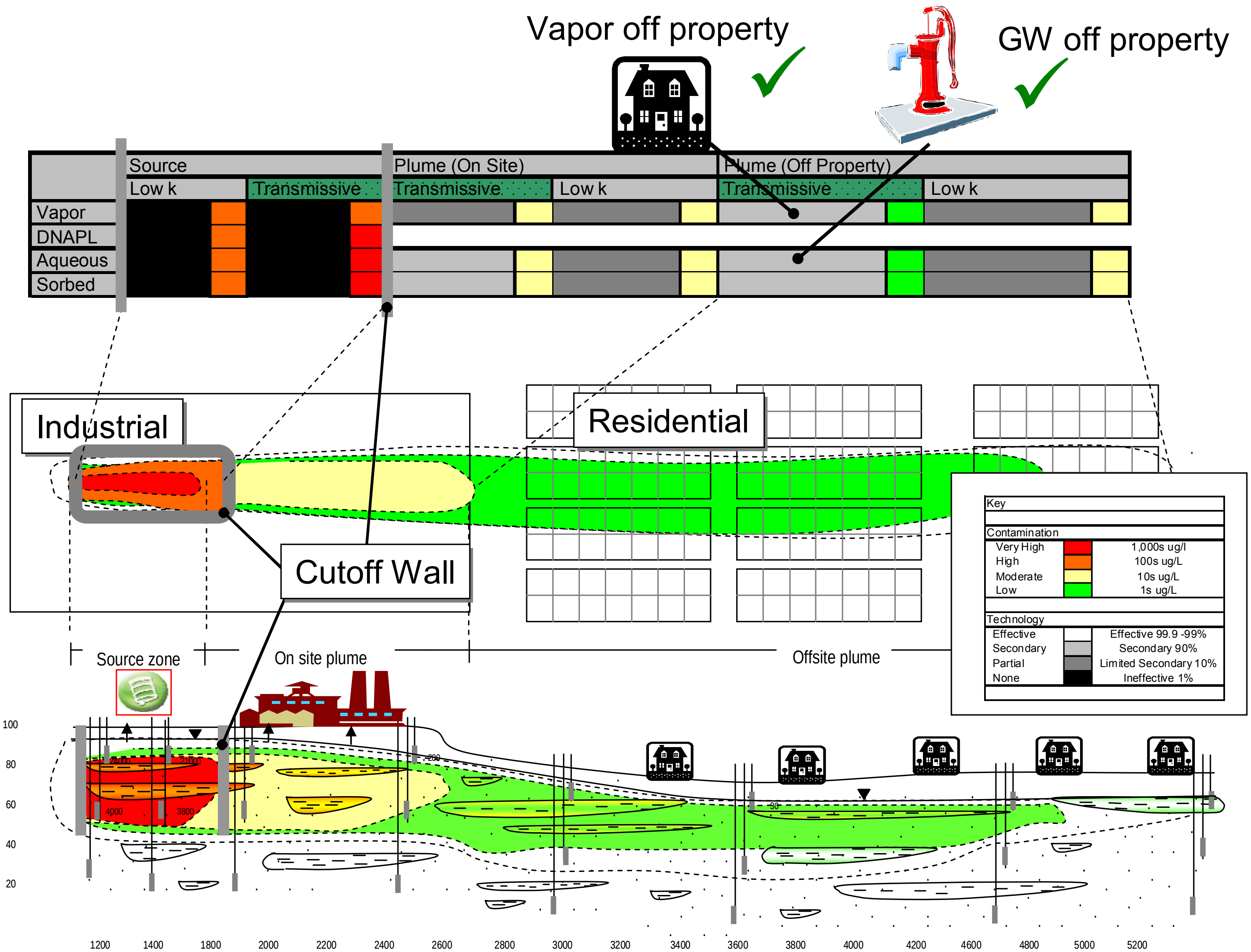
Resource Conservation				
Limit future degradation of resources				
Restore impacted groundwater to standards needed for beneficial use				
Protect sensitive biological habitat				

Source containment with institutional controls for GW



Source Containment + GW Institutional Controls

good | ok | marginal | no eff.

Current Conditions	Protection of human health and the environment	Conservation of natural resources	Address adverse community impacts	Minimize the burden of past practices on future generations
Risk				
Prevent active adverse human or ecological exposure via groundwater	good		good	good
Prevent active adverse human or ecological exposure via soil gas	ok	ok	ok	ok
Prevent adverse worker related exposures via soil, groundwater, and/or soil vapor	marginal		marginal	marginal
Extent				
Prevent expansion of source zones and plumes	good	good	good	good
Reduce the extent of source zones and plumes	ok	ok	ok	ok
Longevity				
Reduce the period in which immobile contaminants in source zones will provide persistent releases to groundwater and/or soils gas.	no eff.	no eff.	no eff.	no eff.
Reduce the period in which immobile contaminants in plume will provide persistent releases to groundwater and/or soils gas.	ok	ok	ok	ok
Regulatory				
Comply with local, state, and federal regulations	marginal	marginal	marginal	marginal
Community				
Address adverse (non-health) impacts to communities	marginal	marginal	marginal	marginal
Land use				
Restore beneficial use of impacted lands		ok	ok	ok
Economic				
Select actions that have a practical near terms capital costs and minimal life cycle cost			good	good
Avoid undue interruptions to communities, government, and industry activities			good	good
Redress adverse impacts to property values		ok	ok	ok
Sustainability				
Select measures that have a net positive environmental benefit	good	good	good	good
Progress to a state in which passive remedies will be sufficient to address residual impacts				marginal
Enhance the effectiveness of complementary technologies				ok
Resource Conservation				
Limit future degradation of resources	good	good	good	good
Restore impacted groundwater to standards needed for beneficial use	marginal	marginal	marginal	marginal
Protect sensitive biological habitat		marginal	marginal	marginal

Other Examples

- Plume without natural attenuation
- Fracture rock without matrix porosity
- Fracture rock with matrix porosity

Closing

Key Points

- Holistic evaluation of all compartments
- The nature of the problem evolves with time
- Goals need to be SMART
- Single Technologies rarely address all compartments
- Many goals compete with each other
- Learning to value what is achievable and live with what remains

Discussion

- Value of compromise
  - Finding ways to go forward with what is beneficial, attainable, and verifiable
  - Learning to live with what will remain
- Alternatives to strict numerical standards
- Challenge of non-degradation policies
- Ways to break the log jam
- Time frames

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

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Development Of A Protocol And Screening Tool For Selection Of DNAPL Remedial Technologies

ER-0424

Carmen A. Lebrón
NAVFAC ESC

Dr. David Major
Dr. Julie Konzuk
Geosyntec Consultants

Dr. Bernard Kueper
Queen's University

Dr. Jason Gerhard
University of Western Ontario

DoD EPA DOE SERDP

ESTCP

Seminar Outline:

Thursday, December 3, 2009		
Start	**End**	**Topic**
10:25 AM	**10:40 AM**	**Background, Objectives and Introduction to Screening Tool Development** *(Presented by Ms. Carmen A. Lebrón)*
10:40 AM	**11:05 AM**	**Numerical Modeling: Simulations && Conclusions/Generalizations from Simulations** *(Presented by Dr. Bernard Kueper)*
11:05 AM	**11:20 AM**	**Conclusions/Generalizations from Case Studies** *(Presented by Dr. Julie Konzuk)*
11:20 PM	**11:30 AM**	**Screening Tool Demonstration** *(Presented by Dr. Julie Konzuk)*
11:30 PM	**11:45 AM**	**Questions & Answers**

DNAPL Remediation Paradigm

- **Uncertainties in DNAPL remediation technology selection:**
  - **How do different technologies perform in various geological/chemical environments?**
  - **What are reasonable expectations in terms of mass removal and concentration reductions?**
  - **What technology best meets our goals/needs?**

Project Objectives

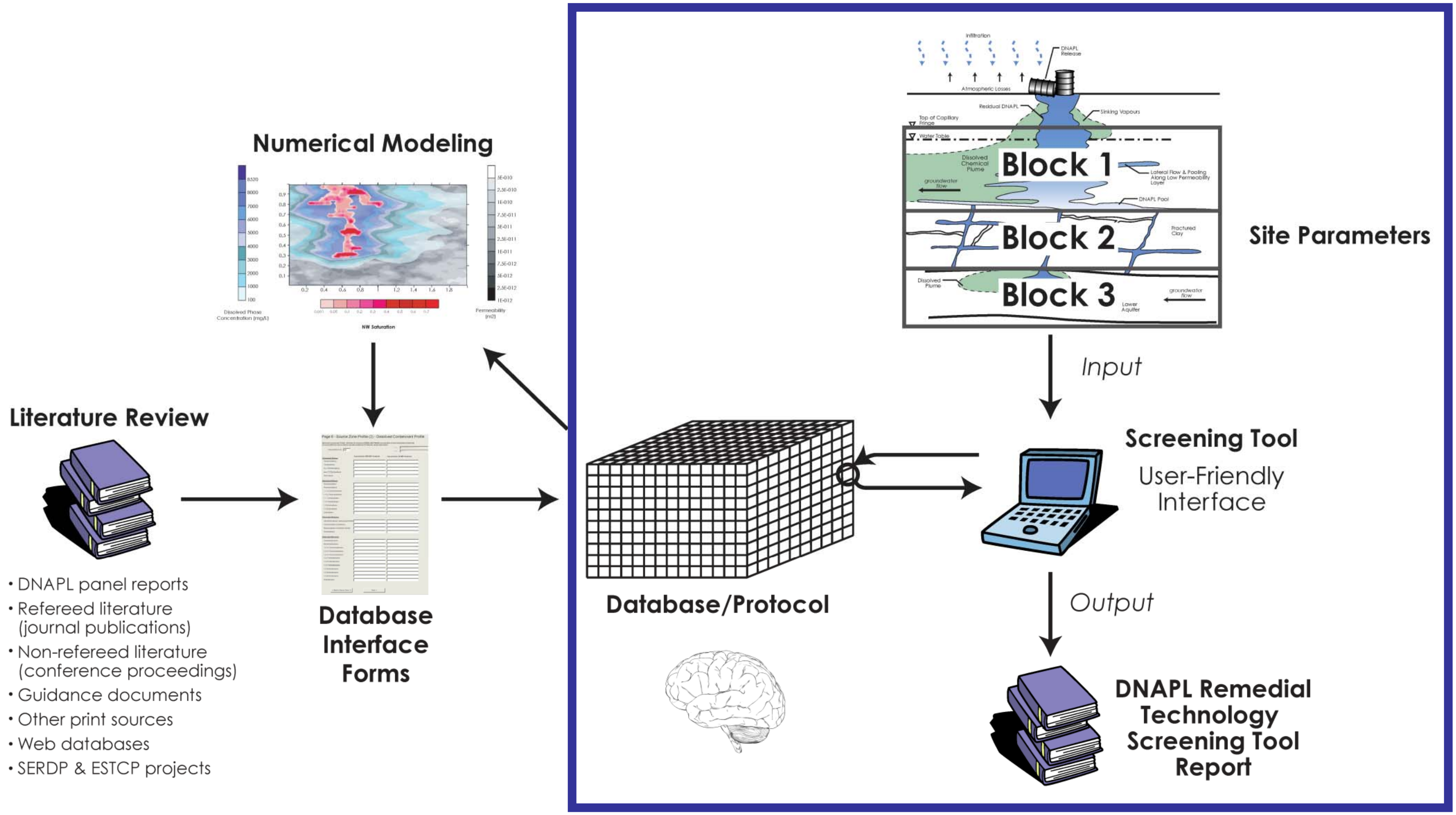
- Develop a screening tool that can be applied at DNAPL source zone sites to:
  - Reduce uncertainty in estimating remedial outcomes
  - Evaluate potential technology performance
  - Aid RPMs in technology selection based on desired performance metrics

- Screening tool developed using a modular approach, which allows for:
  - Incorporating other features in the future
  - Periodic updates of information in the screening tool database without reprogramming the screening tool

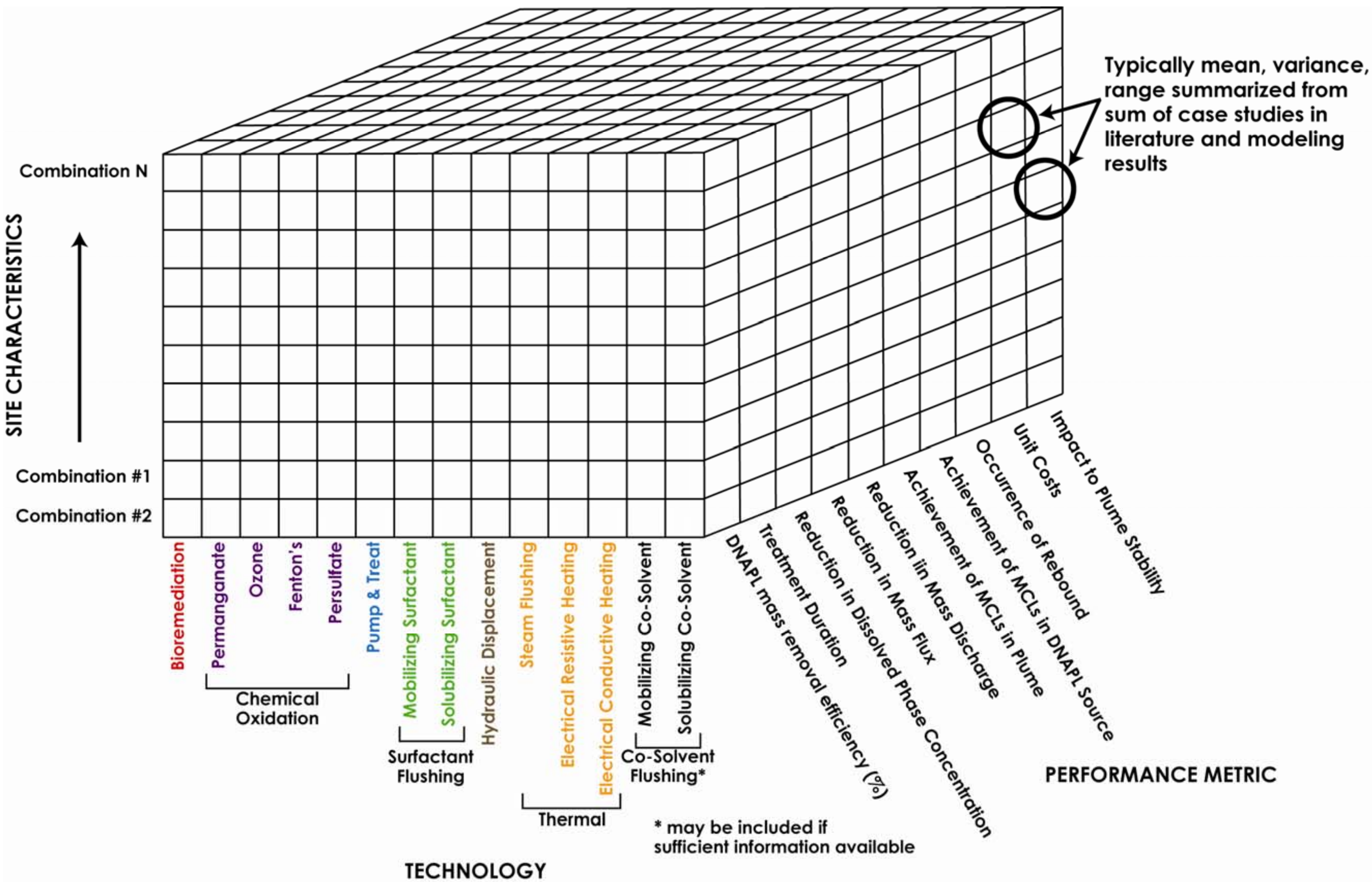
~~Prediction Tool~~

Expectation Management Tool

Technical Approach

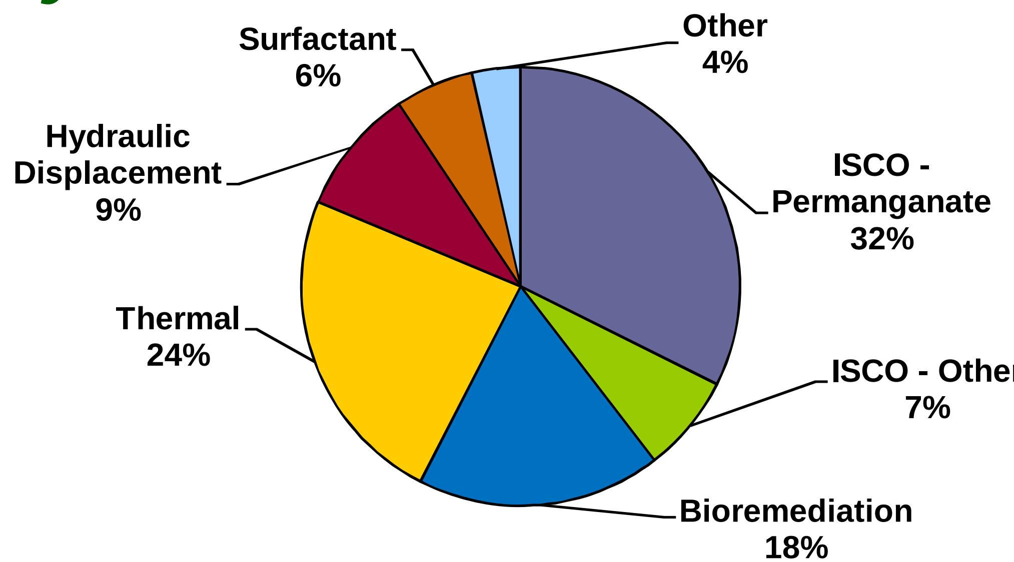


The Matrix, a.k.a. Database

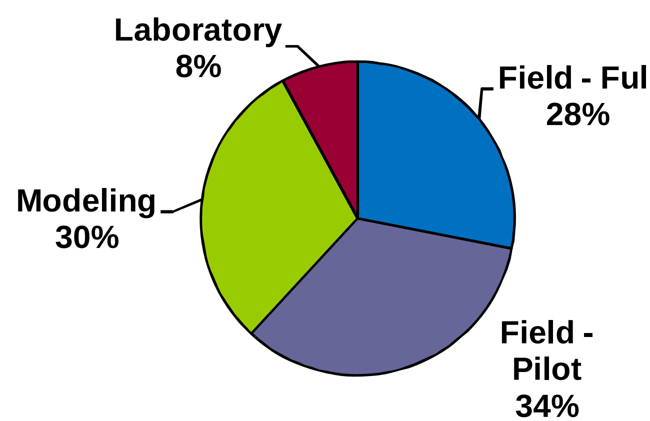


Case Study Collection

- Case studies entered into database to date:
  - 42 modeling case studies
  - 11 lab studies
  - 86 field case studies

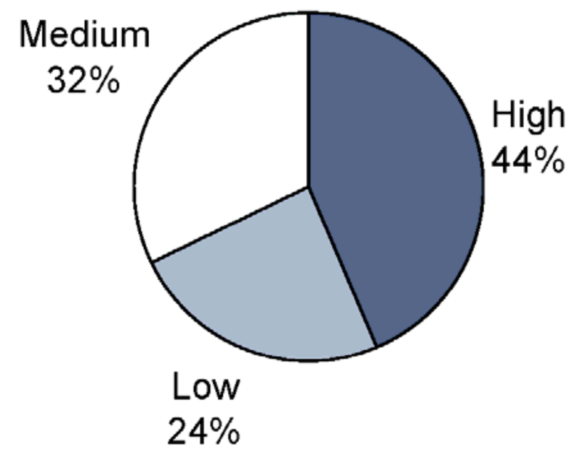


- An additional 76 field case studies identified and >70 modeling case studies still to be entered into database



Case Study Quality Control

- **Data Quality Rankings (DQRs) developed for each case study**
  - ♦ **Value between 1 (low) and 3 (high)**

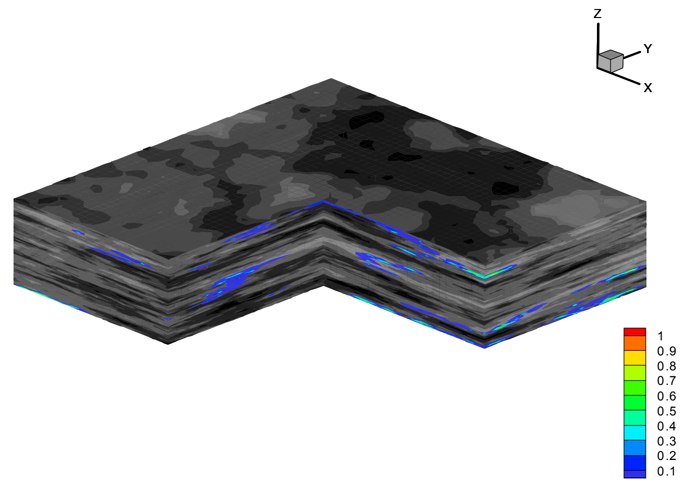


- **Weighted average of ratings for:**
  - ♦ **Information source (low weighting)**
  - ♦ **Age of study (medium)**
  - ♦ **Methods used to characterize DNAPL (medium)**
  - ♦ **Completeness of pre-treatment data set (high)**
  - ♦ **Completeness of post-treatment data set (high)**
- **In screening tool, users can filter data based on DQRs**

Modeling/Simulations

- ✓ ***Why Modeling?***

- ✓ ***Allows us to:***

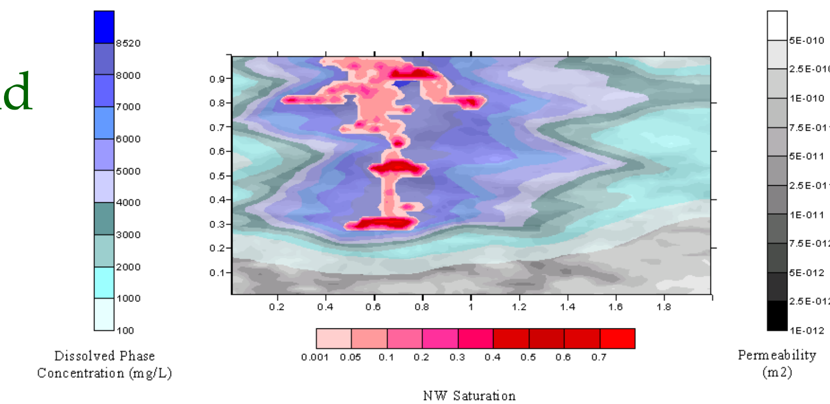


- ♦ **Simulate DNAPL releases in various geologic settings and create different architectures**
- ♦ **Compare technology performance**
- ♦ **Evaluate impact of various factors on tech performance**
- ♦ **Assess source removal long-term impacts on groundwater quality**

Modeling/Simulations

Step 1. Creating template sites

- Simulate a range of geological, hydrogeological, and chemical environments
- Simulate a range of DNAPL releases and architectures



Step 2. Modeling DNAPL Treatment

- Simulate treatment with selected technologies
- Metrics evaluated include DNAPL mass reduction, source zone concentration reduction, mass flux reduction, plume length

Template Site	+	Remediation Technology	=	Case study in Screening Tool

Simulations/Template Sites

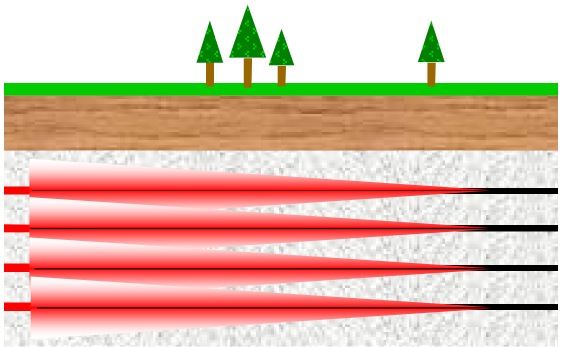
Porous Media Template Site Parameters

Template Site	DNAPL Type	DNAPL Release Volume	Hydraulic Conductivity	Soil Heterogeneity
Low Heterogeneity	TCE	7.57 m^3	10^{-3} cm/s	**ln k = 1**
Low K	TCE	7.57 m^3	**10^{-4} cm/s**	ln k = 2
Low DNAPL Volume	TCE	**1.89 m^3**	10^{-3} cm/s	ln k = 2
Lower Density DNAPL	**1,1,1-TCA**	7.57 m^3	10^{-3} cm/s	ln k = 2
Base Case	**TCE**	**7.57 m^3**	**10^{-3} cm/s**	**ln k = 2**
Higher Density DNAPL	**PCE**	7.57 m^3	10^{-3} cm/s	ln k = 2
High DNAPL Volume	TCE	**18.9 m^3**	10^{-3} cm/s	ln k = 2
High K	TCE	7.57 m^3	**10^{-2} cm/s**	ln k = 2
High Heterogeneity	TCE	7.57 m^3	10^{-3} cm/s	**ln k = 4**

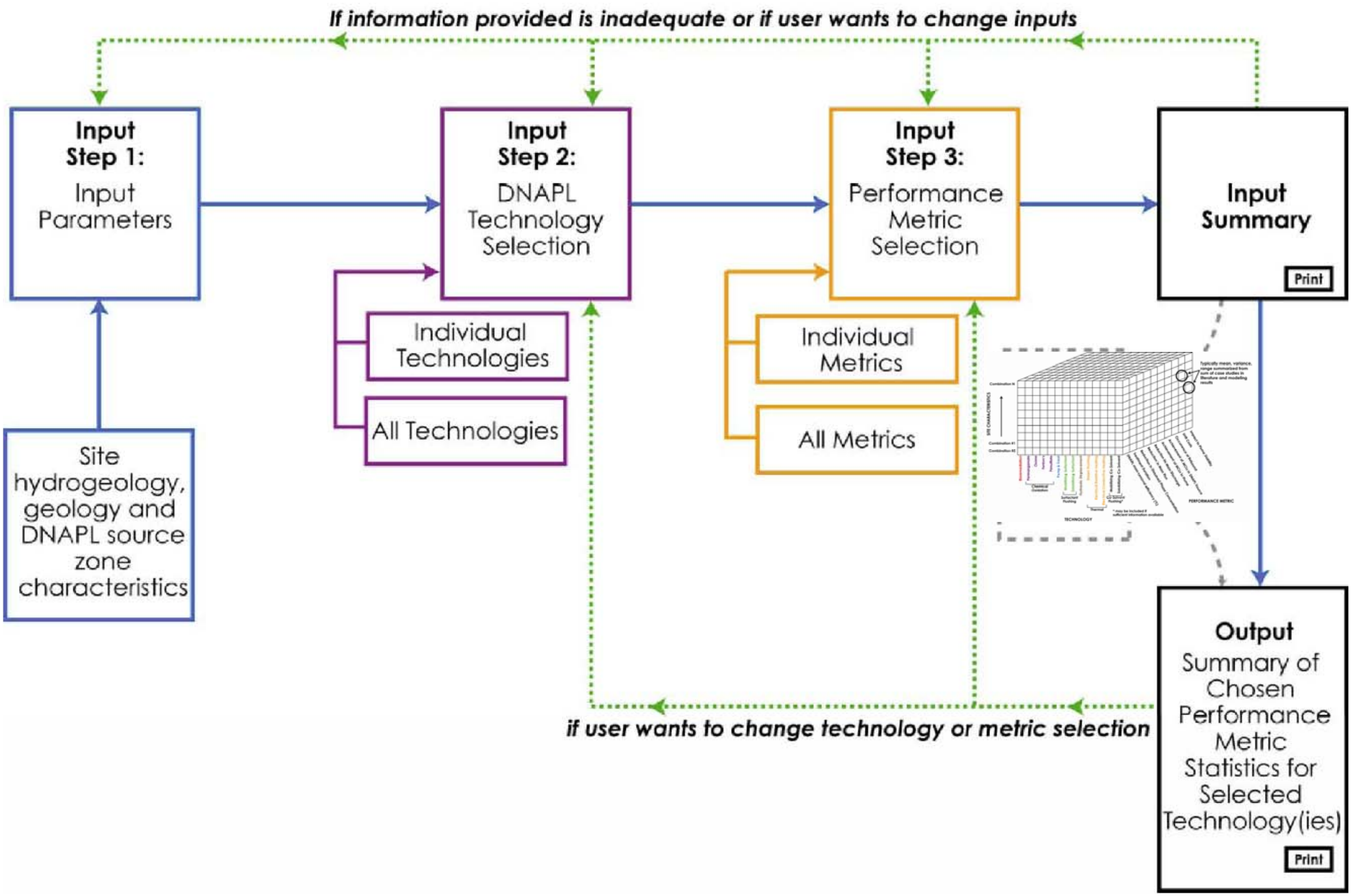
Simulations/Template Sites

Fractured Clay Template Site Parameters

Template Site	DNAPL Type	Fracture Aperture	Matrix Porosity	Fraction Organic Carbon	Fracture Spacing
Low Organic Carbon	TCE	75 µm	30%	**0.0015**	1.0 m
Low Matrix Porosity	TCE	75 µm	**15%**	0.003	1.0 m
Low Fracture Aperture	TCE	**37.5 µm**	30%	0.003	1.0 m
Low Density DNAPL	**1,1,1-TCA**	-	-	-	-
Base Case	**TCE**	**75 µm**	**30%**	**0.003**	**1.0 m**
High Density DNAPL	**PCE**	75 µm	30%	0.003	1.0 m
High Fracture Aperture	TCE	**150 µm**	30%	0.003	1.0 m
High Matrix Porosity	TCE	75 µm	**45%**	0.003	1.0 m
High Organic Carbon	TCE	75 µm	30%	**0.006**	1.0 m

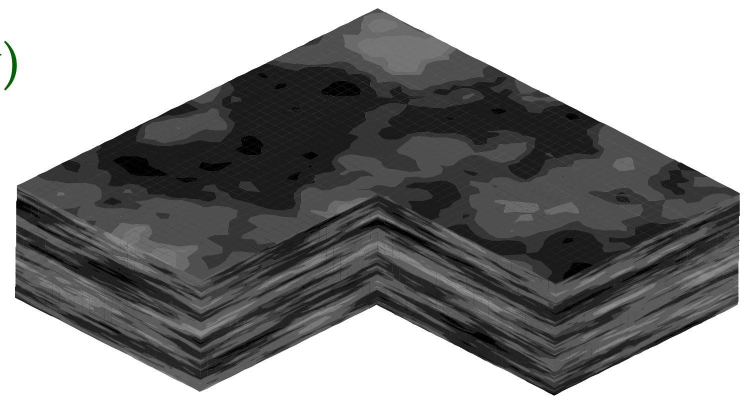


Screening Tool Structure

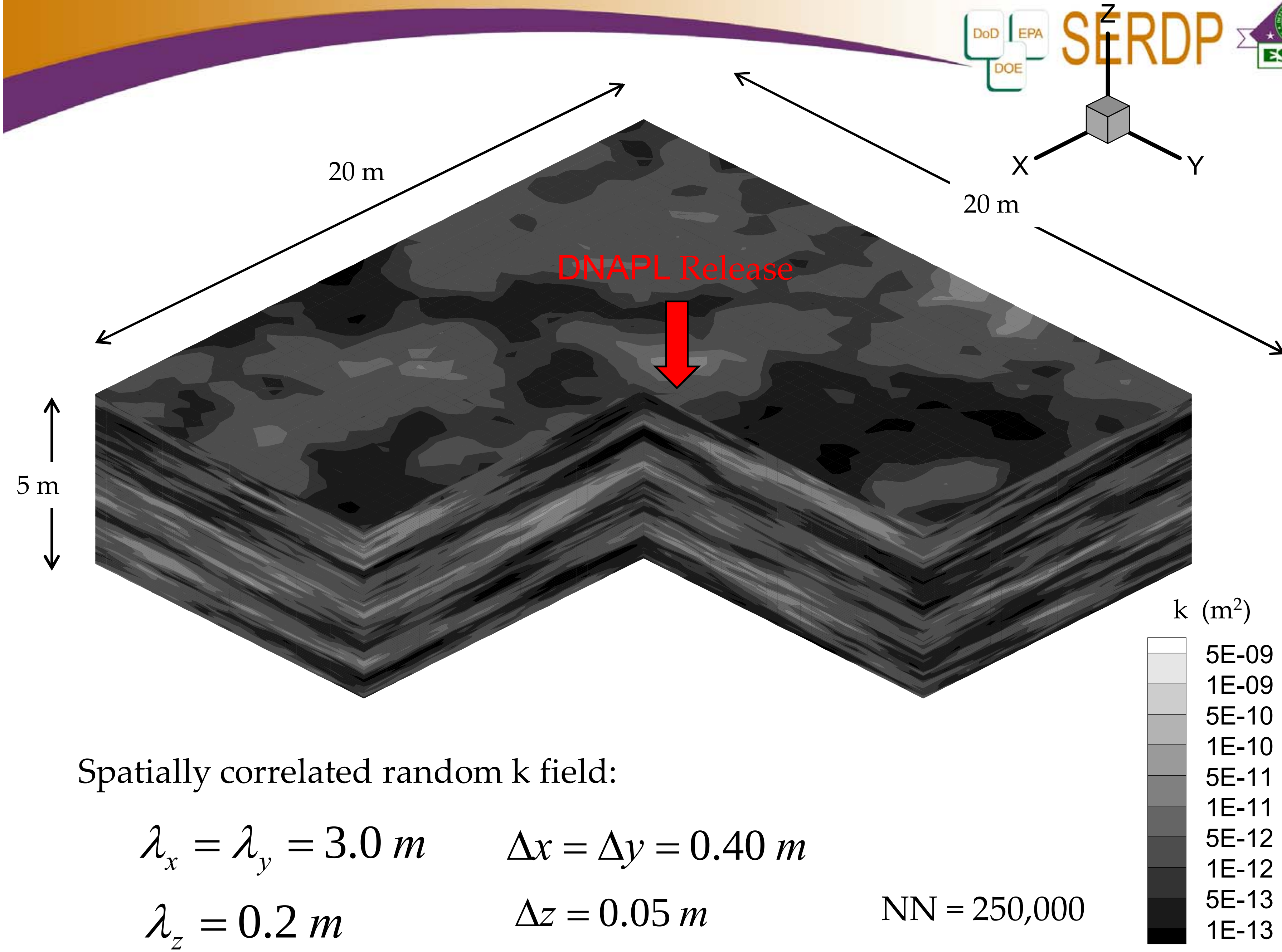


Numerical Modeling

- Numerical simulation of DNAPL source zone remediation in porous and fractured media
- Technologies considered:
  - Hydraulic Displacement (PM only)
  - Pump-and-Treat
  - In Situ Chemical Oxidation
  - Enhanced In Situ Bioremediation
  - Surfactant Flushing



- Technologies applied to 'Template Sites'



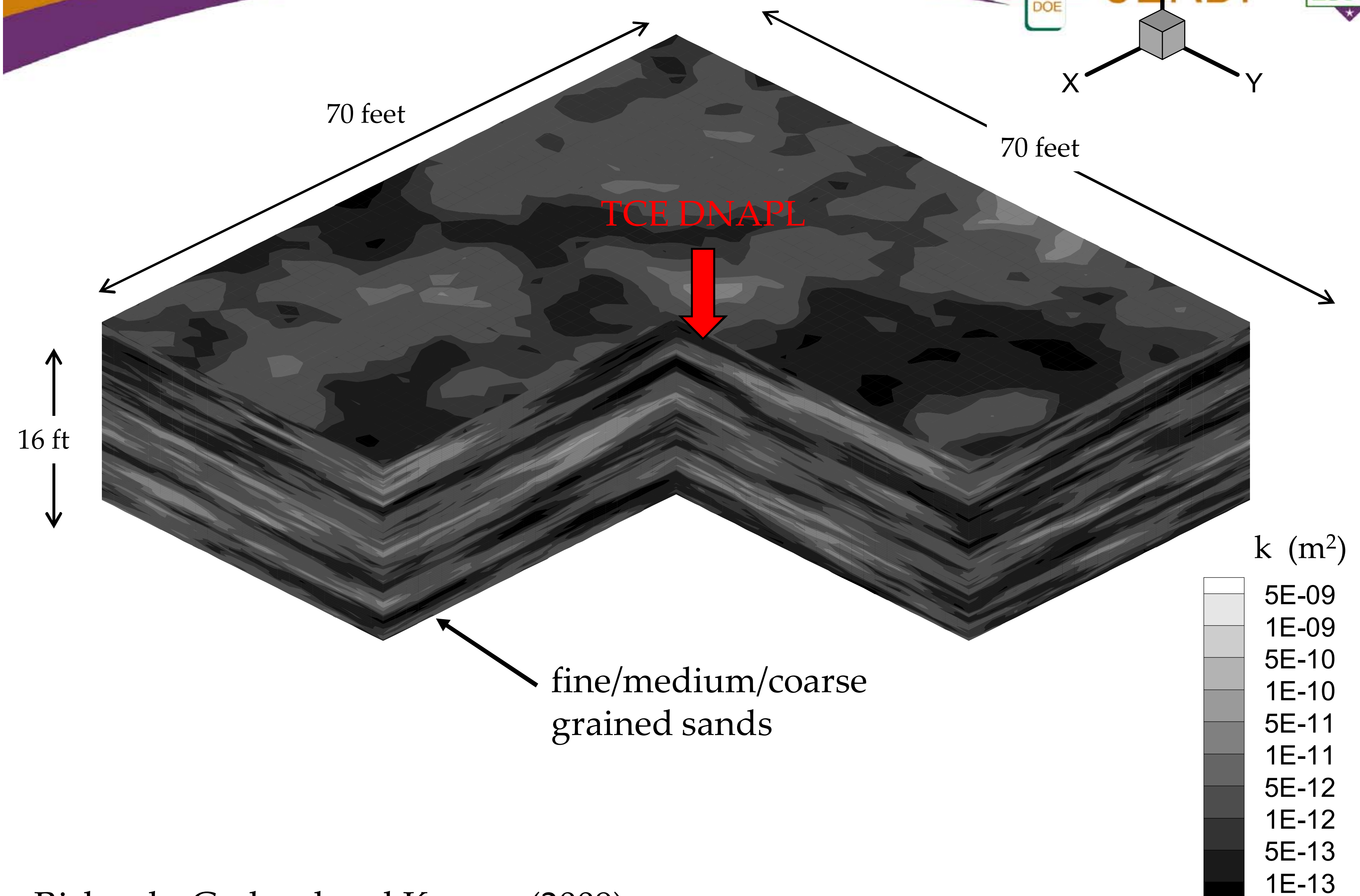
Spatially correlated random k field:

$$\lambda_x = \lambda_y = 3.0\ m \qquad \Delta x = \Delta y = 0.40\ m$$

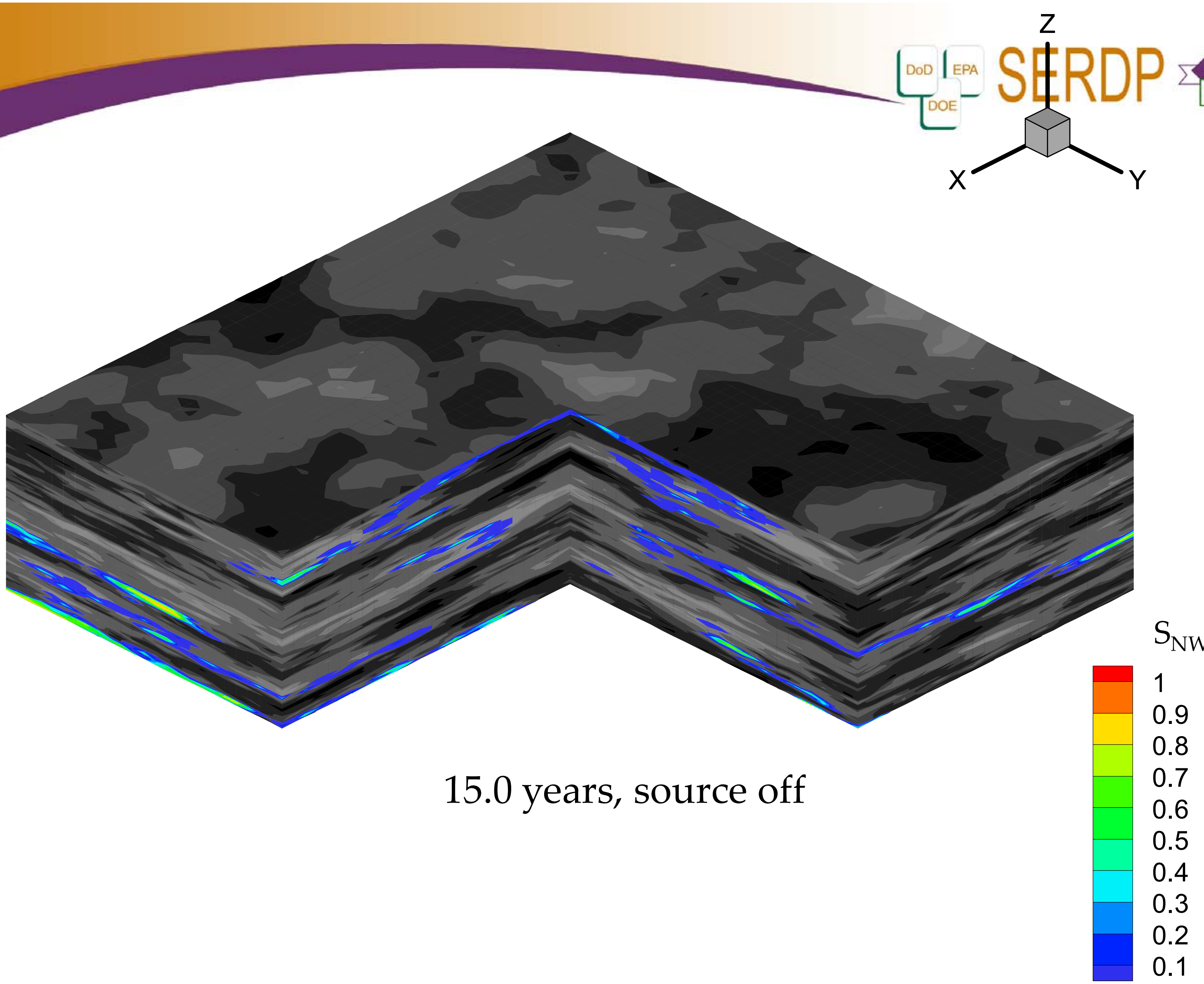
$$\lambda_z = 0.2\ m \qquad \Delta z = 0.05\ m \qquad \mathrm{NN} = 250{,}000$$

Porous Media Template Sites

Template Site	DNAPL	Initial Mass (kg)	Initial Volume (m^3)	Mean *k* (m^2)	Variance ln *k*
Base case	TCE	3520	2.41	$3.03\ 10^{-12}$	1.74
High mean k	TCE	3496	2.39	$3.02\ 10^{-11}$	1.74
Low mean *k*	TCE	3535	2.42	$3.04\ 10^{-13}$	1.74
Low heterogeneity	TCE	3355	2.30	$1.87\ 10^{-12}$	0.87
High heterogeneity	TCE	3186	2.18	$7.41\ 10^{-12}$	3.48
Small DNAPL volume (post HD)	TCE	785	0.54	$3.03\ 10^{-12}$	1.74
Small DNAPL volume (pre HD)	TCE	803	0.55	$3.03\ 10^{-12}$	1.74
Large DNAPL volume	TCE	7343	5.03	$3.03\ 10^{-12}$	1.74
High density DNAPL	PCE	3871	2.37	$3.03\ 10^{-12}$	1.74



Richards, Gerhard and Kueper (2009)



15.0 years, source off

Remediation Model Development & Application

DNAPL3D

Dissolution

RT3D
(modified)

<u>Testing & Calibration</u>
-analytical
-column experiments

<u>System Specific Characteristics</u>
-reaction kinetics
-species and initial conditions
-clogging effects

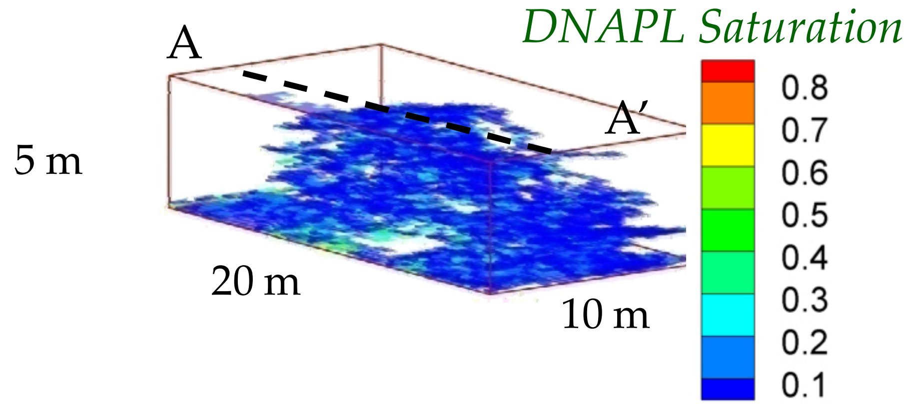
DNAPL3D-RX
(remediation model)

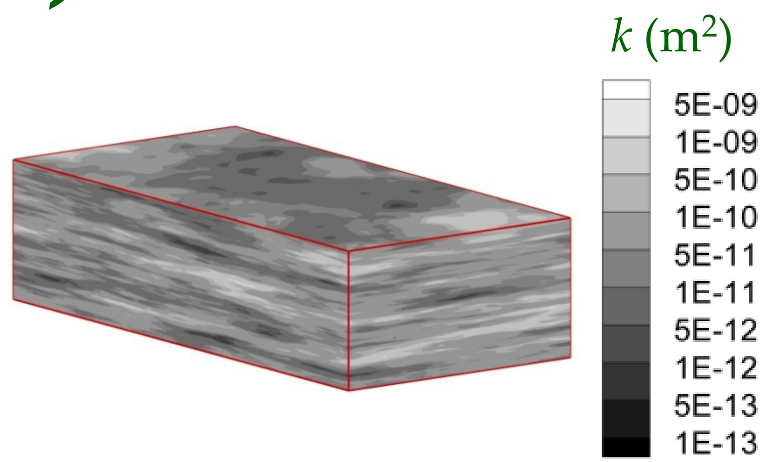
<u>Field Scale Applications</u>

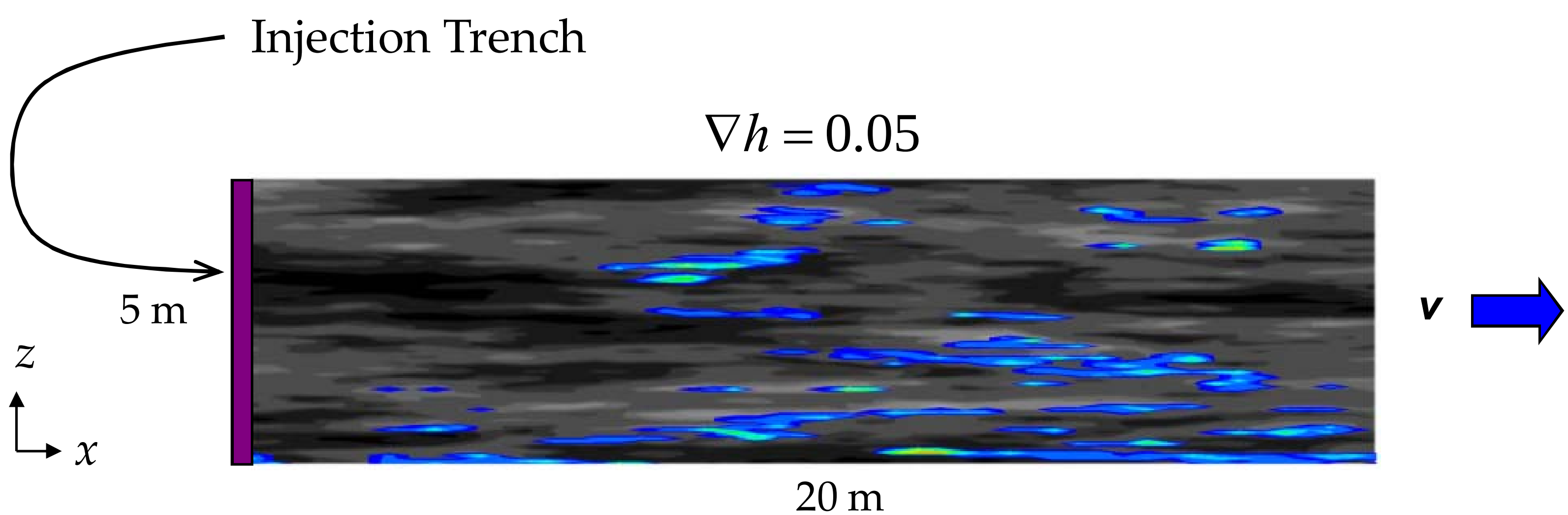
9 Template Sites (geology, TCE/PCE/111-TCA, DNAPL volume)

5 technologies (HD, P&T, ISCO, EISB, SEAR)

Base Case Modeling Domain (Template Site 1)







Cross-Section A-A′

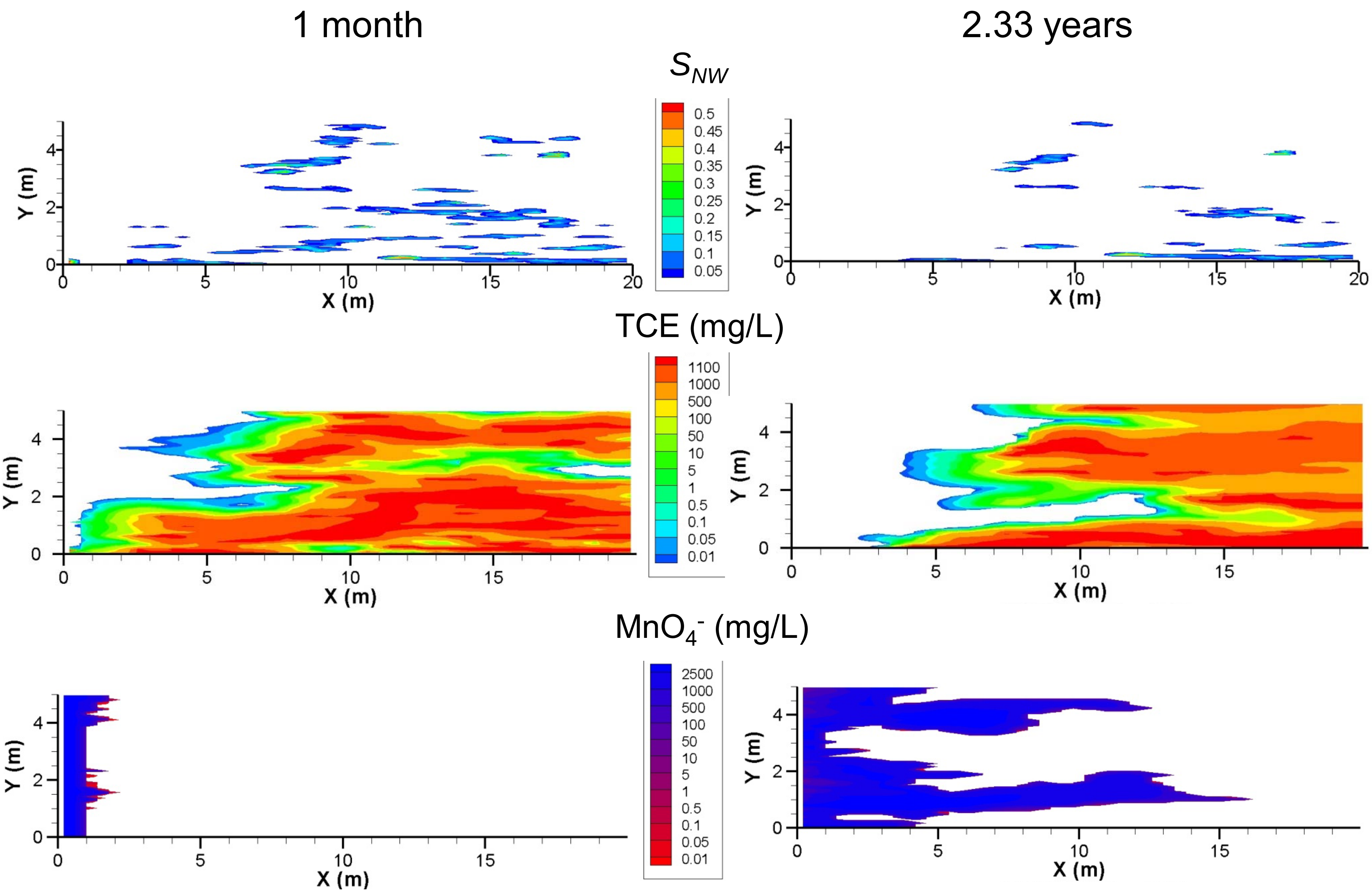
In-Situ Chemical Oxidation (ISCO) with Potassium Permanganate

- Stoichiometry, kinetics and rate constants from literature
- 2nd order reactions for TCE/PCE and OAM with MnO_4^-
- $KMnO_4$ injected at 2,500 mg/L
- Species specific diffusion coefficients (TCE and MnO_4^-)
- OAM cross-correlated with *k* (negative)
- Pore clogging due to rind formation (*West et al., 2008, AWR*)
- Perfectly buffered system assumed
- Local equilibrium dissolution of DNAPL

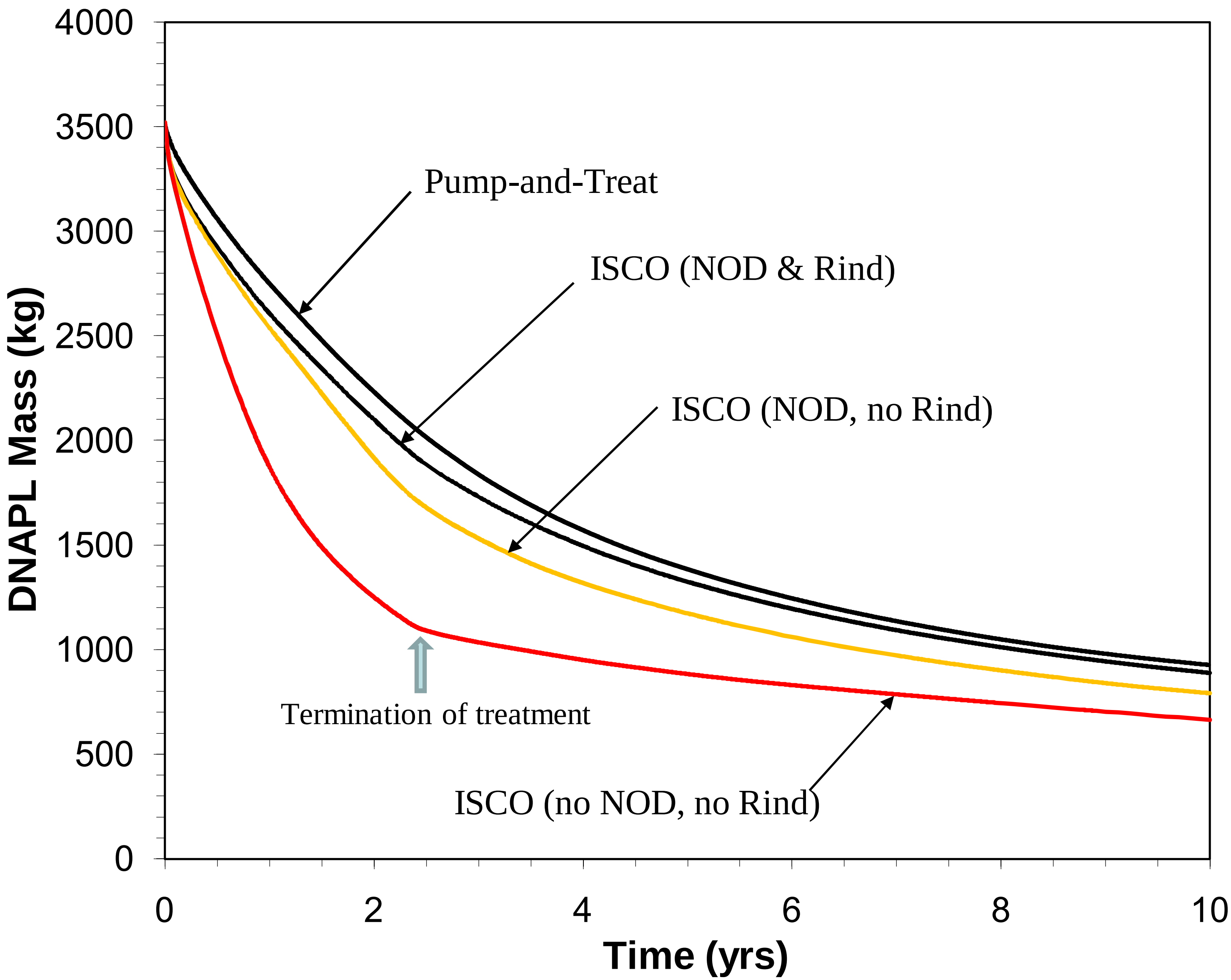
ISCO Simulations

Simulation	Description	Injection Duration (days)	$KMnO_4$ Breakthrough at Exit Face?
1	Base case	849	No
2	High mean *k*	83	No
3	Low mean *k*	3650	No
4	Low heterogeneity	1086	No
5	High heterogeneity	575	No
6a	Small DNAPL volume (post HD)	163	No
6b	Small DNAPL volume (pre HD)	166	No
7	Large DNAPL volume	2251	Yes
8	PCE DNAPL	724	No
9	Base case, no Rind	849	No
10	Base case, no NOD	849	Yes
11	Base case, no NOD & no Rind	849	Yes

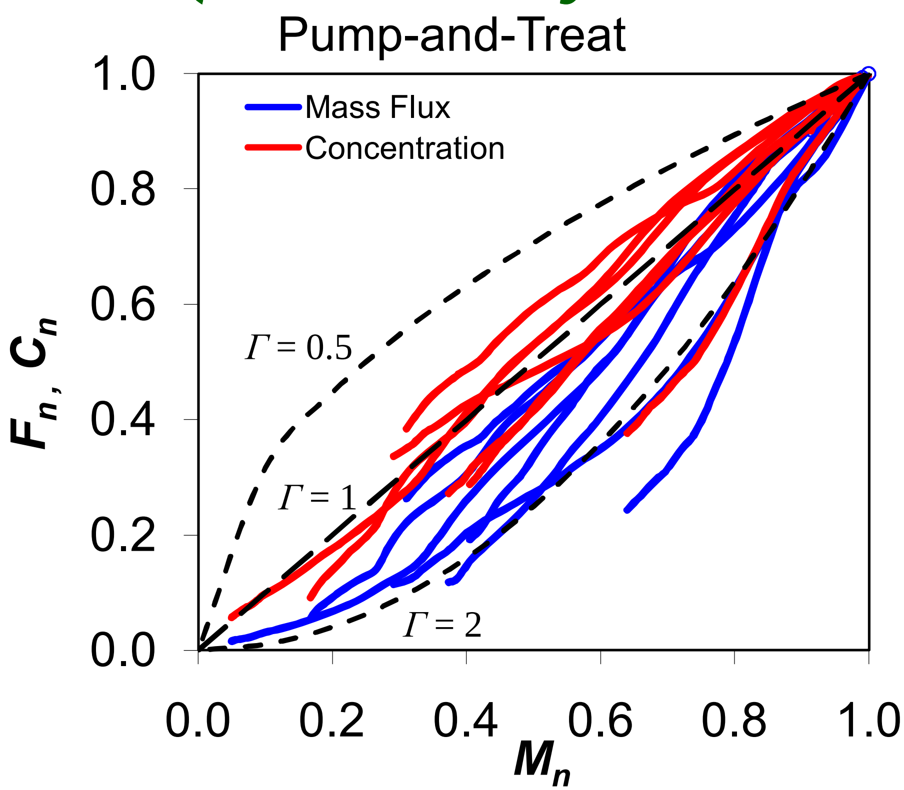
Comparison of ISCO Output – Base Case

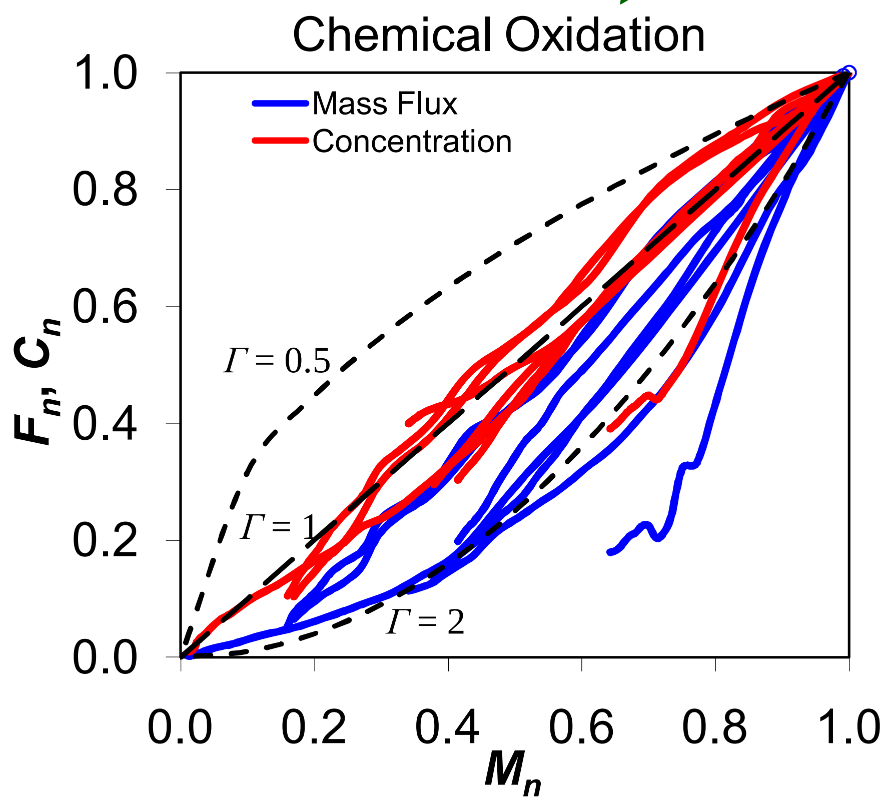


ISCO Base Case Template



Pump-and-Treat vs Chemical Oxidation (Boundary Flux and Concentration)





$$C_n = \frac{C(t)}{C(t_0)} \qquad F_n = \frac{M_f(t)}{M_f(t_0)} \qquad M_n = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right) \qquad C_n = \frac{C(t)}{C(t_0)} = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right)^{\Gamma}$$

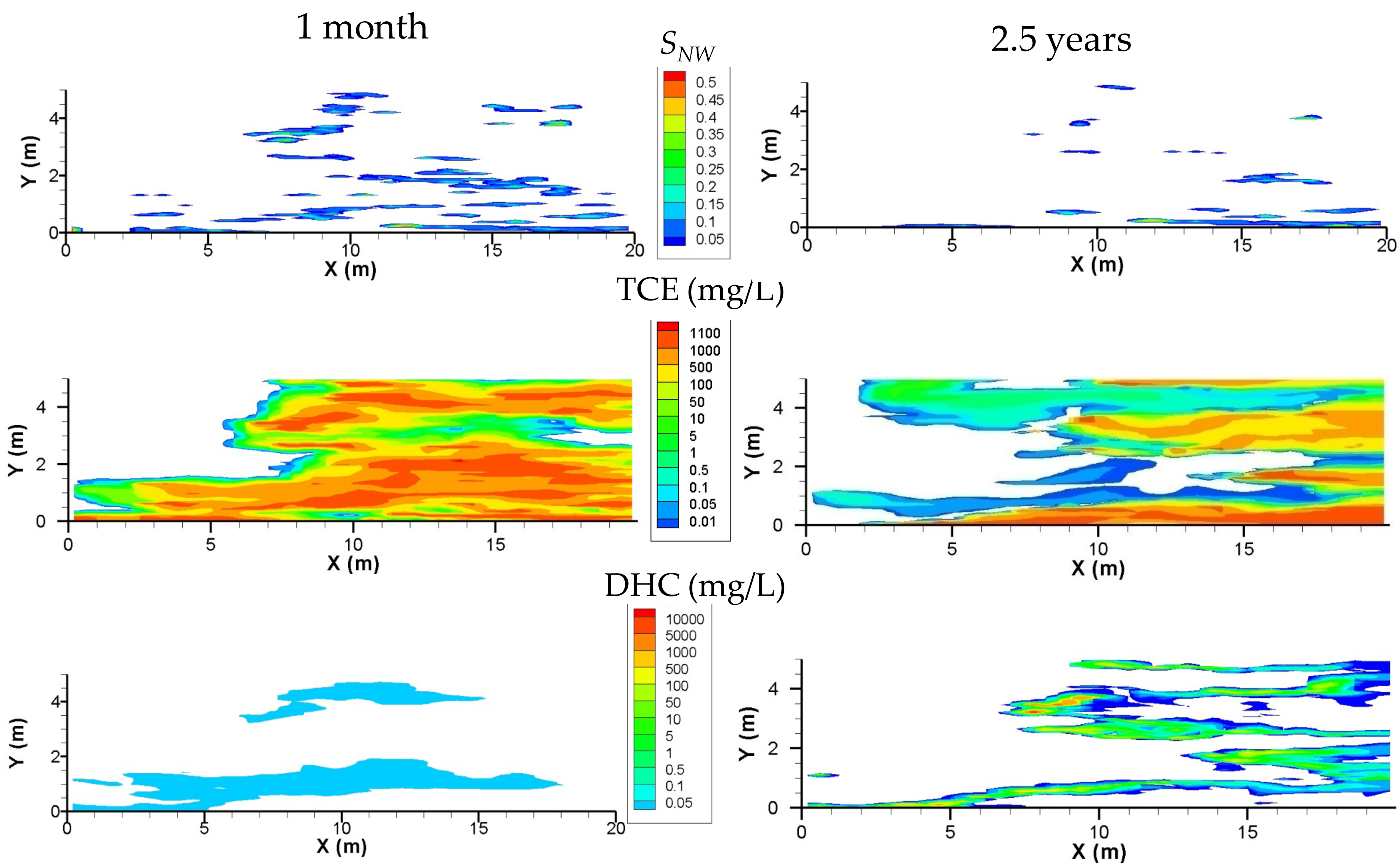
Enhanced In-Situ Bioremediation (EISB)

- **Stochiometry, kinetics and rate constants from literature**
- **TCE (or PCE) degrades to *cis*-DCE**
- **Monod-type kinetics**
- **First-order decay of biomass**
- **Lactate injected @ 1 day/week for 2.5 years**
- **3 biologic species: fermentors, dechlorinators, & methanogens (competitors)**
- **All microbes initially uniformly distributed**
- **Lactate converted to H_2 by fermentors**
- **H_2 consumed by both dechlorinators & methanogens**
- **Bioclogging due to dechlorinator & methanogen biomass**

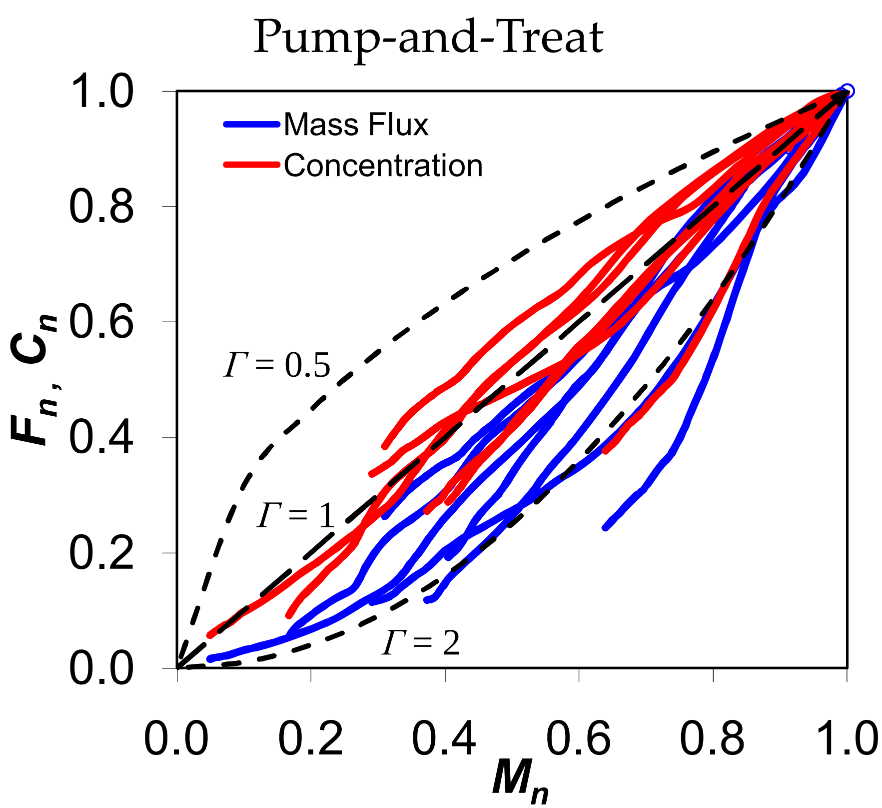
EISB Simulations

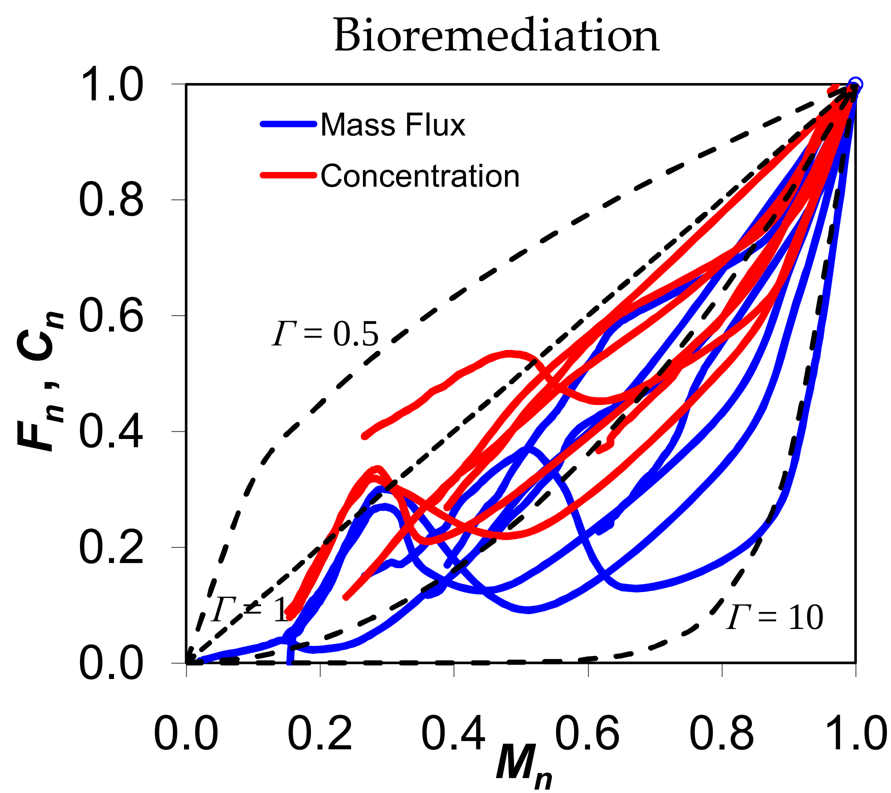
Simulation	Description	Lactate injection concentration (mg/L)
1	Base case	39130
2	High mean *k*	39130
3	Low mean *k*	39130
4	Low heterogeneity	39130
5	High heterogeneity	39130
6a	Small DNAPL volume (post HD)	39130
6b	Small DNAPL volume (pre HD)	39130
7	High DNAPL volume	39130
8	PCE DNAPL	39130 or 7511
BC1	Base case, no bioclogging	39130
BC2	Base case, no competition	39130
BC3	Base case, no bioclogging & no competition	39130
PS1	Base case, 1 hour/day lactate pulse	134160
PS2	Base case, 1 week/month lactate pulse	24113

Comparison of EISB Output – Base Case



Pump-and-Treat v. Bioremediation (boundary flux and concentration)





$$C_n = \frac{C(t)}{C(t_0)} \qquad F_n = \frac{M_f(t)}{M_f(t_0)} \qquad M_n = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right) \qquad C_n = \frac{C(t)}{C(t_0)} = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right)^{\Gamma}$$

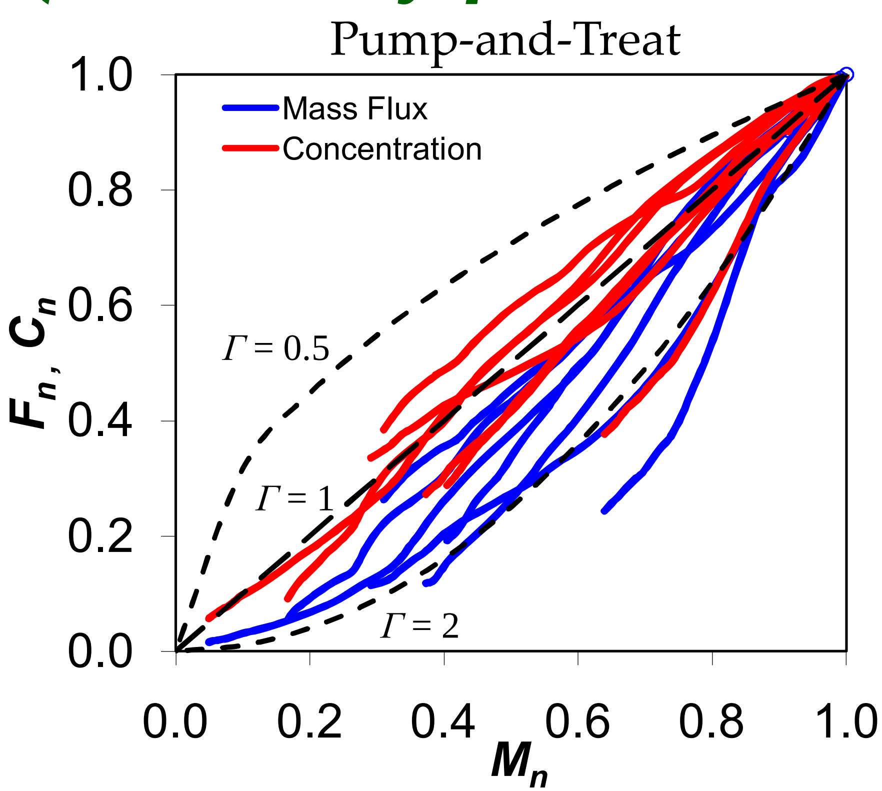
Surfactant Enhanced Aquifer Remediation (SEAR)

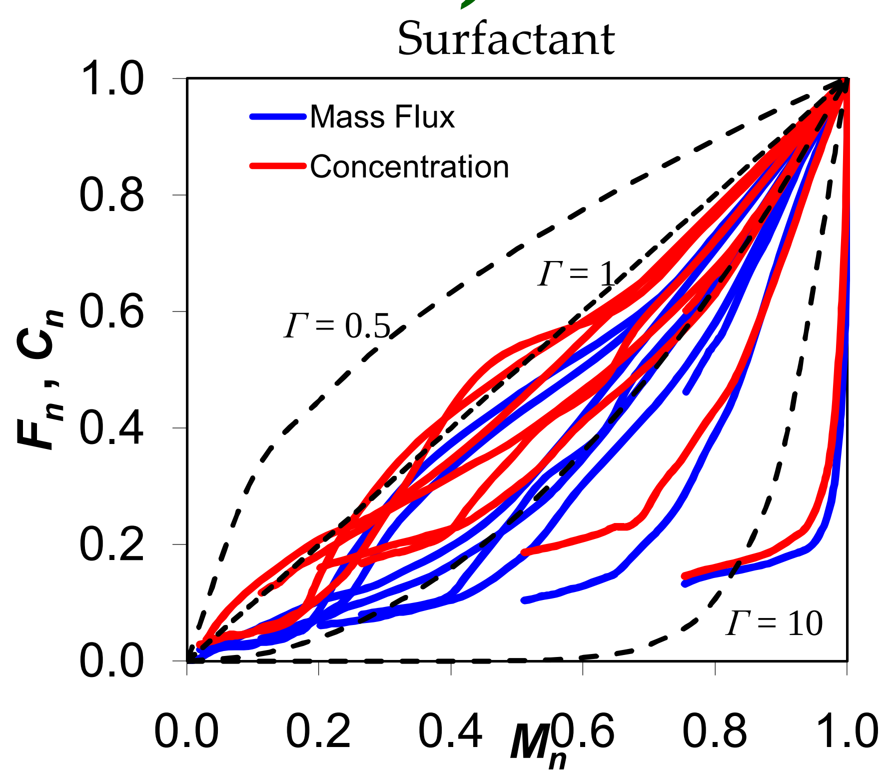
- **Dissolution kinetics and rate constants from literature**
- **Tween 80 injected at 40,000 mg/L for 22 days (base case)**
- **3 species: TCE/PCE solute, Tween 80 micelles, and pseudo micro-emulsion**
- **Enhanced dissolution by linear driving function**
- **Interfacial tension reduction not simulated**
- **Model tested against published column experiments**

SEAR Simulations

Simulation	Template site	SEAR injection time (days)
1	Base case (TCE)	22
2	High mean *k*	2
3	Low mean *k*	223
4	Low heterogeneity	29
5	High heterogeneity	11
6a	Small DNAPL volume (post-HD)	5
6b	Small DNAPL volume (pre-HD)	5
7	Large DNAPL volume	48
8	PCE DNAPL	35

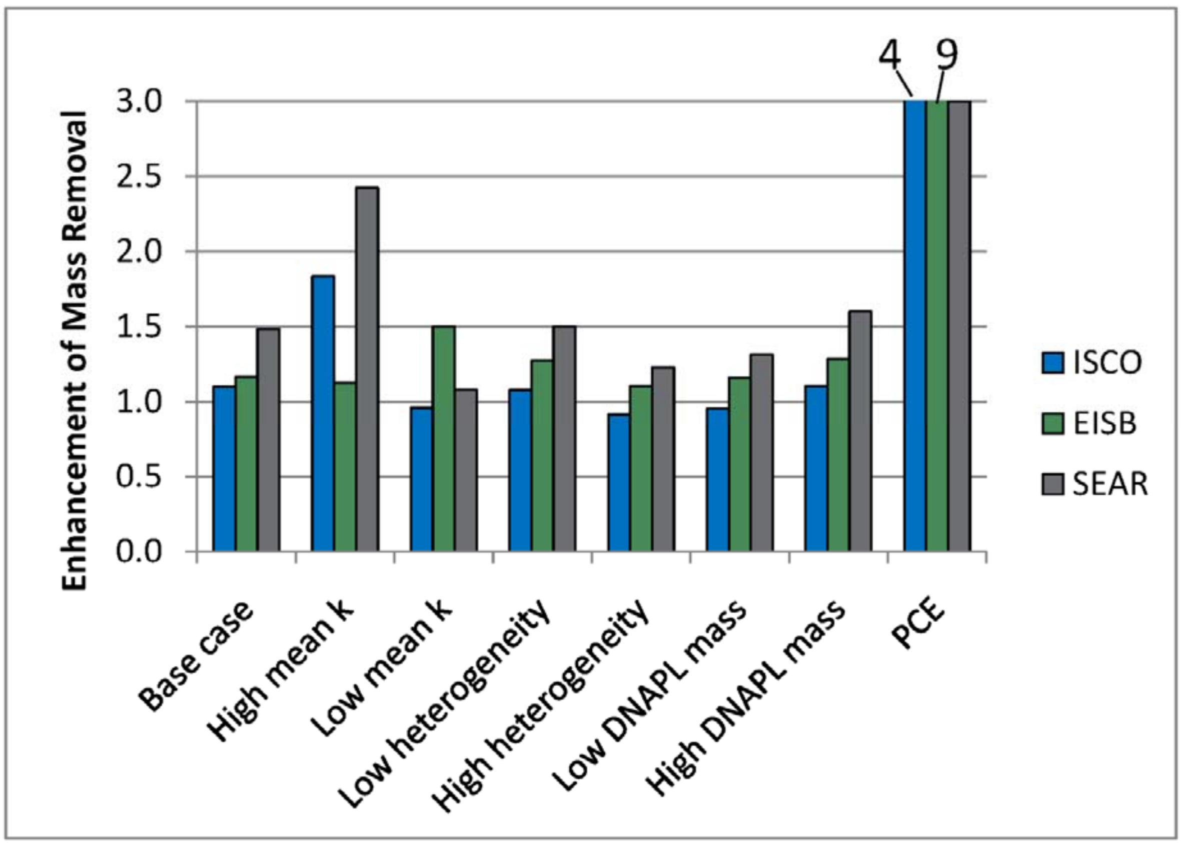
Pump-and-Treat vs SEAR (boundary flux and concentration)





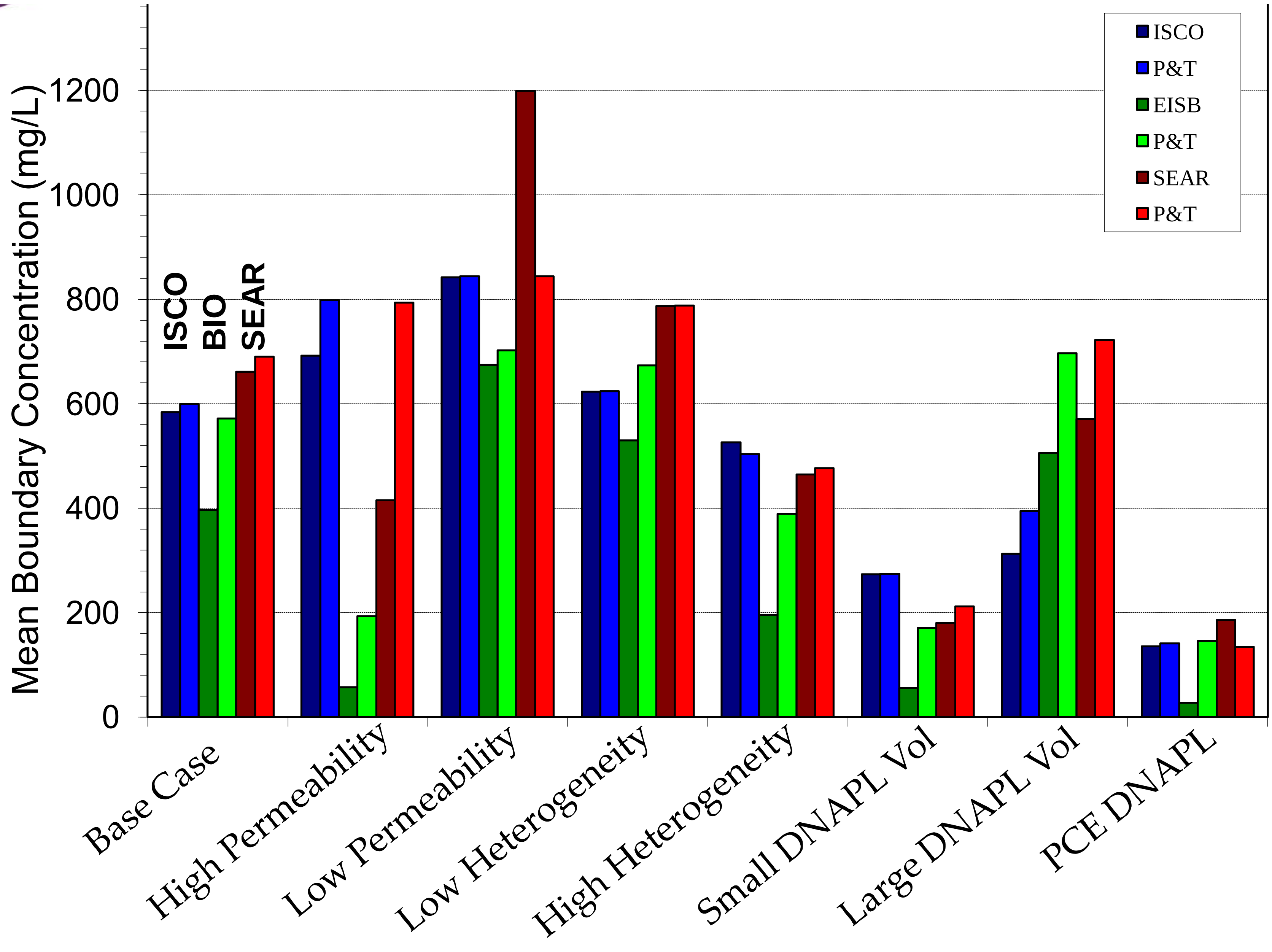
$$C_n = \frac{C(t)}{C(t_0)} \qquad F_n = \frac{M_f(t)}{M_f(t_0)} \qquad M_n = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right) \qquad C_n = \frac{C(t)}{C(t_0)} = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right)^{\Gamma}$$

Comparative Enhancement of DNAPL Mass Removal at End of Treatment

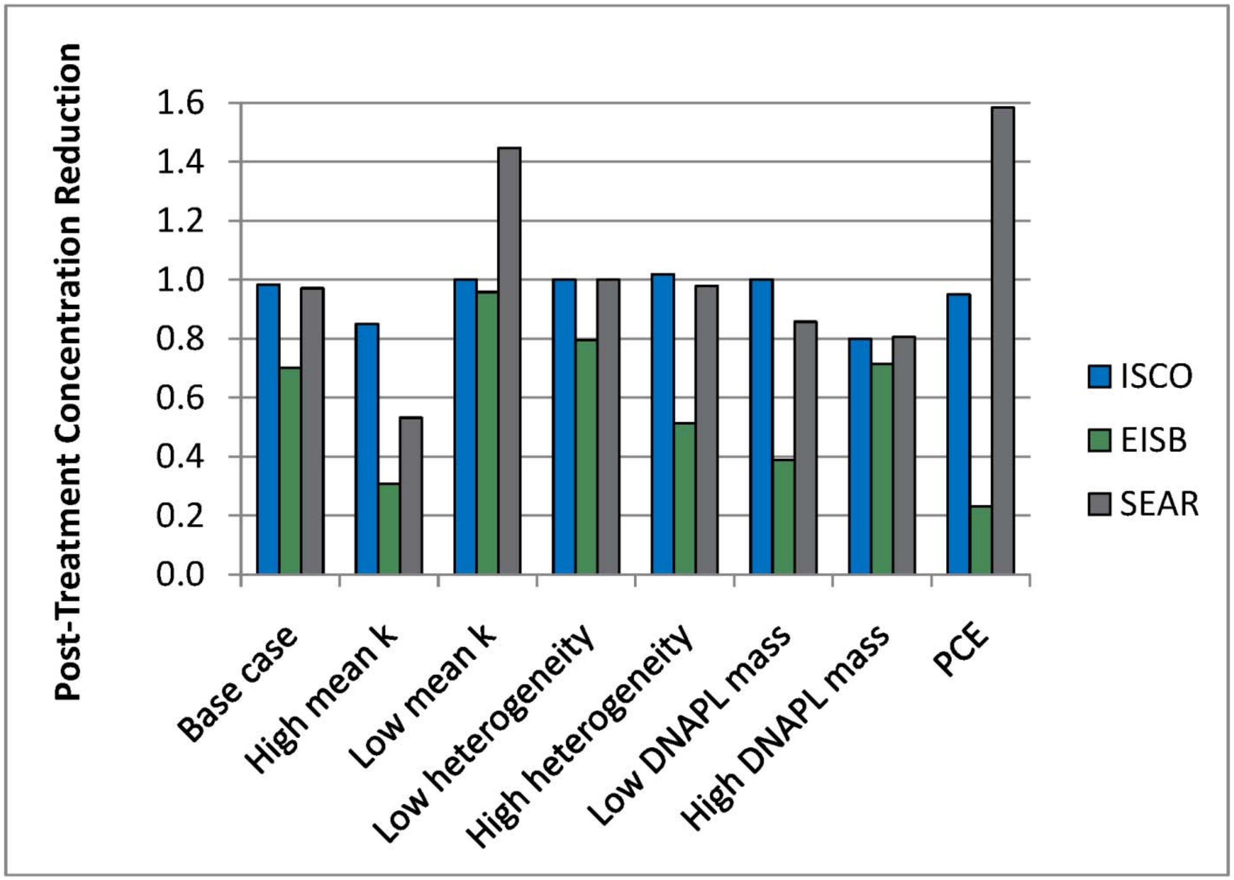


- Enhancement of mass removal greatest where dissolution is not a significant mass removal factor:
  - Lower solubility DNAPLs (PCE)
- ISCO (MnO4) only technology where incomplete treatment reduces mass removal efficiency below doing P&T

Mean Boundary Concentration at End of Treatment

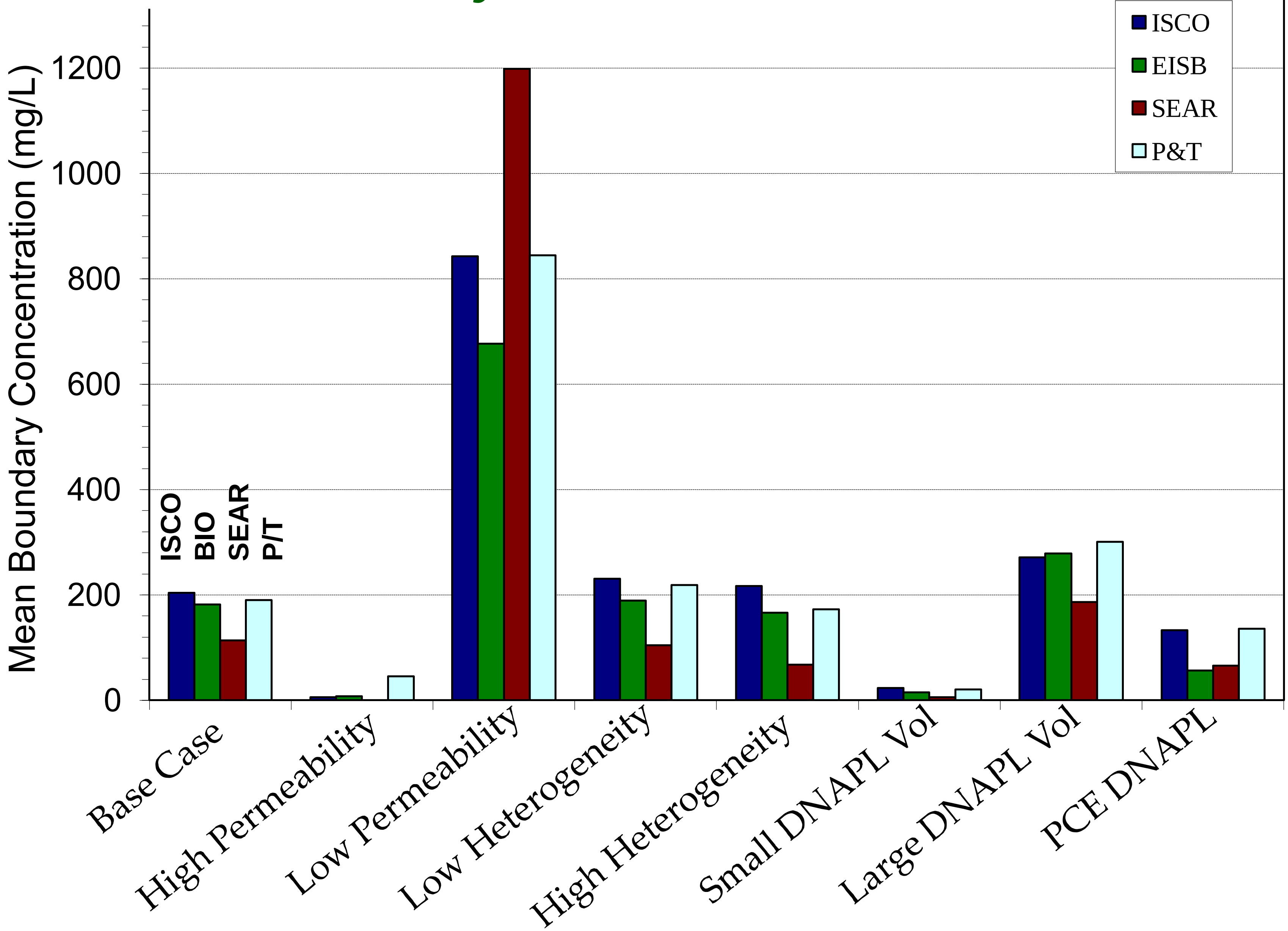


Concentration Reduction Enhancement Normalized to P&T – at End of Treatment

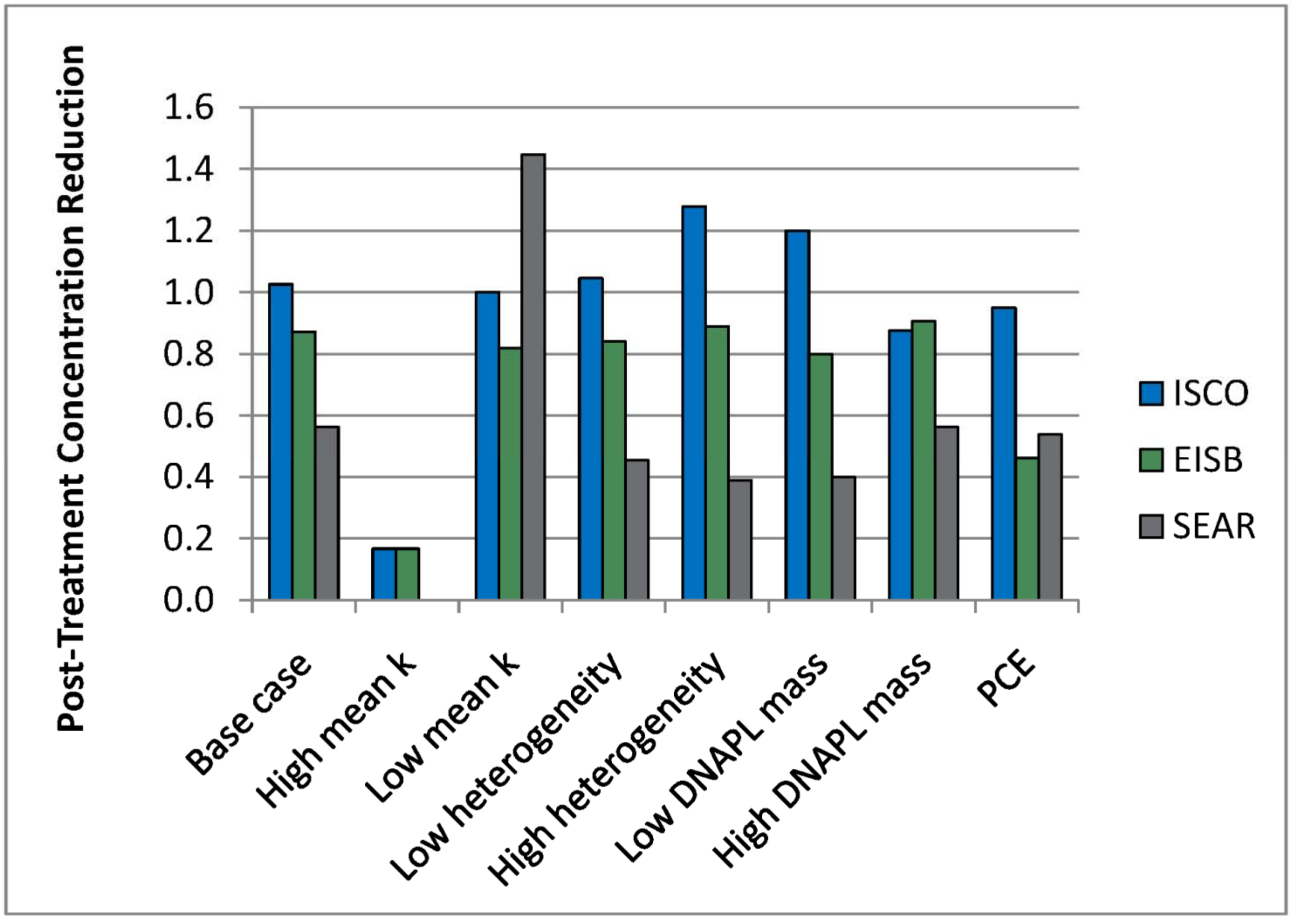


- Reduction factor >1 = concentrations higher than seen for dissolution only
- EISB has greatest enhancement in concentration reductions at treatment termination
- ISCO reductions were minimal

Mean Boundary Concentration
t = 10 years



Concentration Reduction Enhancement Beyond P&T – After 10 Years



- SEAR enhancement of concentration reduction continues to improve, except for low permeability soils
- EISB concentrations still lower than P&T for all, but enhancement in reduction is reduced
- ISCO enhancement still minimal, and worsened in some cases

Conclusions – Porous Media Modeling

- Technology performance (DNAPL mass, flux and concentration reduction) is site specific (geology, DNAPL volume)
- Flux decreases faster than concentration
- Low permeability generally not conducive to injection technologies
- Important to arrive at accurate estimate of DNAPL mass to optimize design

Conclusions – Porous Media Modeling

- P/T & ISCO (MnO_4) typically lead to near-linear reduction in concentration with mass removal, while EISB and SEAR have greater proportion of concentration reduction with DNAPL mass removal
- Partial mass removal will not achieve MCLs in groundwater concentrations
- Demand from natural organic matter can result in significantly more oxidant demand compared to stoichiometric DNAPL mass requirements
  - Cost issue

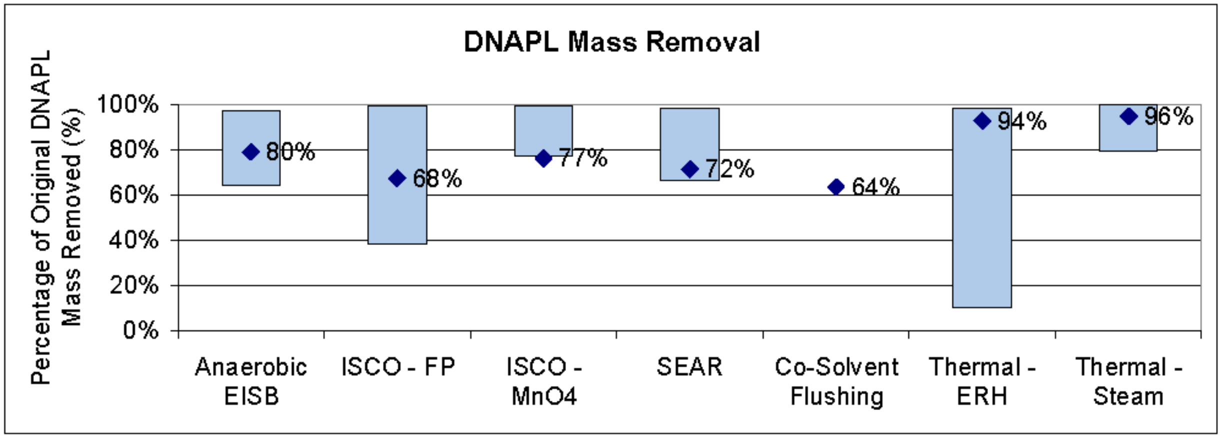
Case Study Trend Analysis

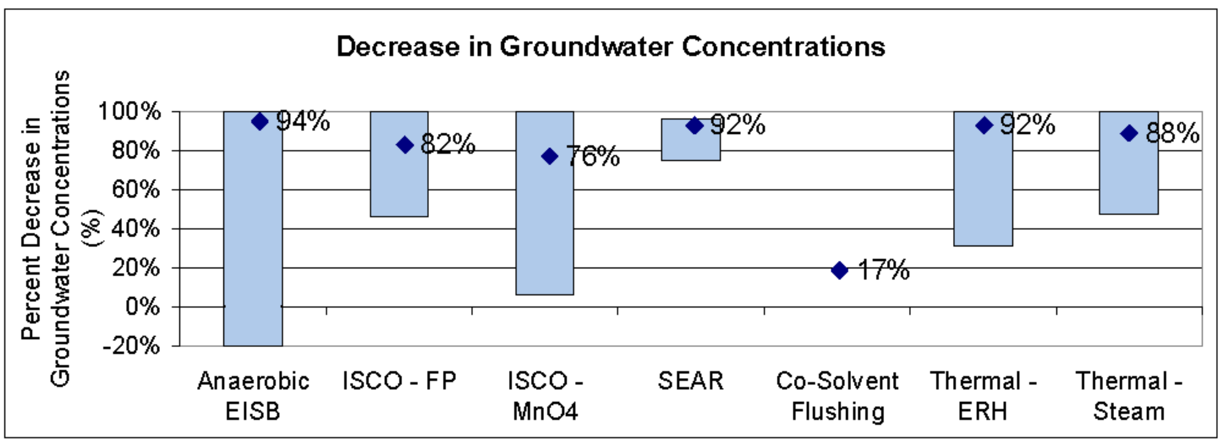
- Linear and non-linear multivariate regression used to evaluate influence of site parameters on technology performance:
  - Correlations between site parameters and performance metrics
  - Determine the 'key' site & technology parameters correlated to performance

Performance Metric	Treatment Area	Saturated Thickness	Soil Heterogeneity	Pooled DNAPL	Electrode Spacing
Decrease in Groundwater Concentrations	*Equally good performance in nearly all case studies*				
Decrease in Soil Concentrations	– – –			– –	
Removal of DNAPL Mass	– – – –				
Treatment Duration (ERH)		++			++++
Treatment Duration (Steam)	+++		++++		
Rebound of Groundwater Concentrations	*Equally good performance in all case studies*				
Unit Cost ($/m^3$)		+++		++	
Achievement of MCLS	*No apparent influence from site parameters*				

– indicates weakest negative correlation, – – – – indicates strongest negative correlation
+ indicates weakest positive correlation, ++++ indicates strongest positive correlation

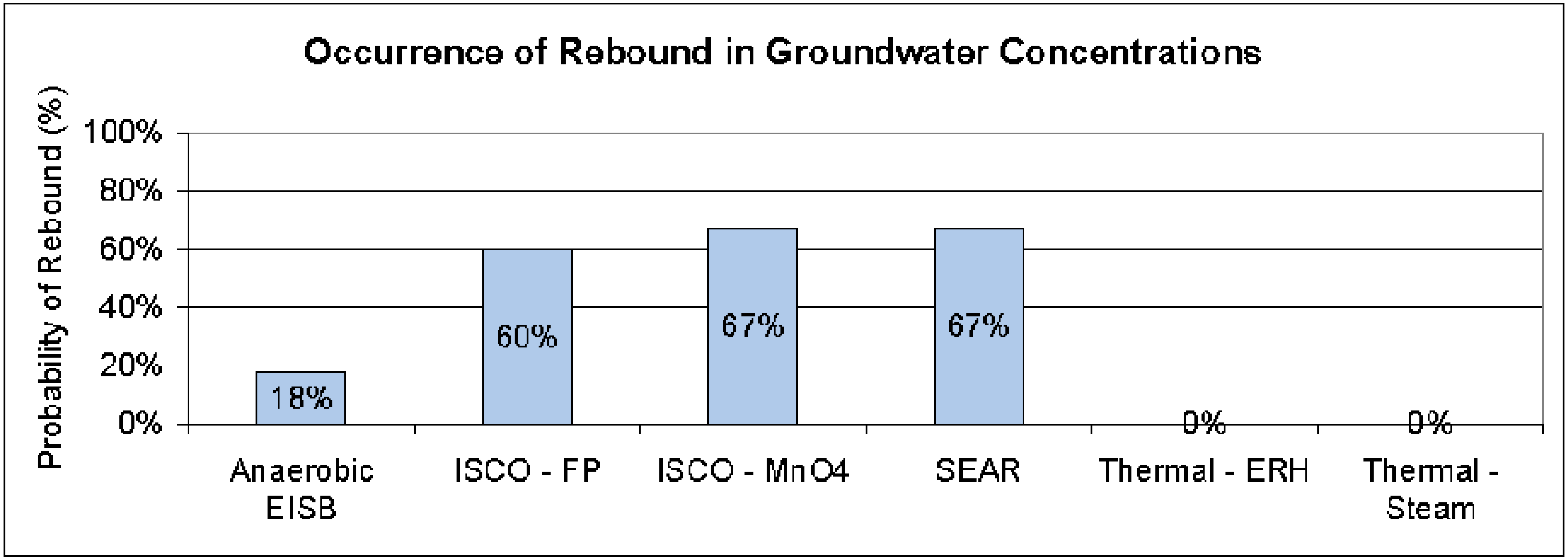
Technology Performance Comparison





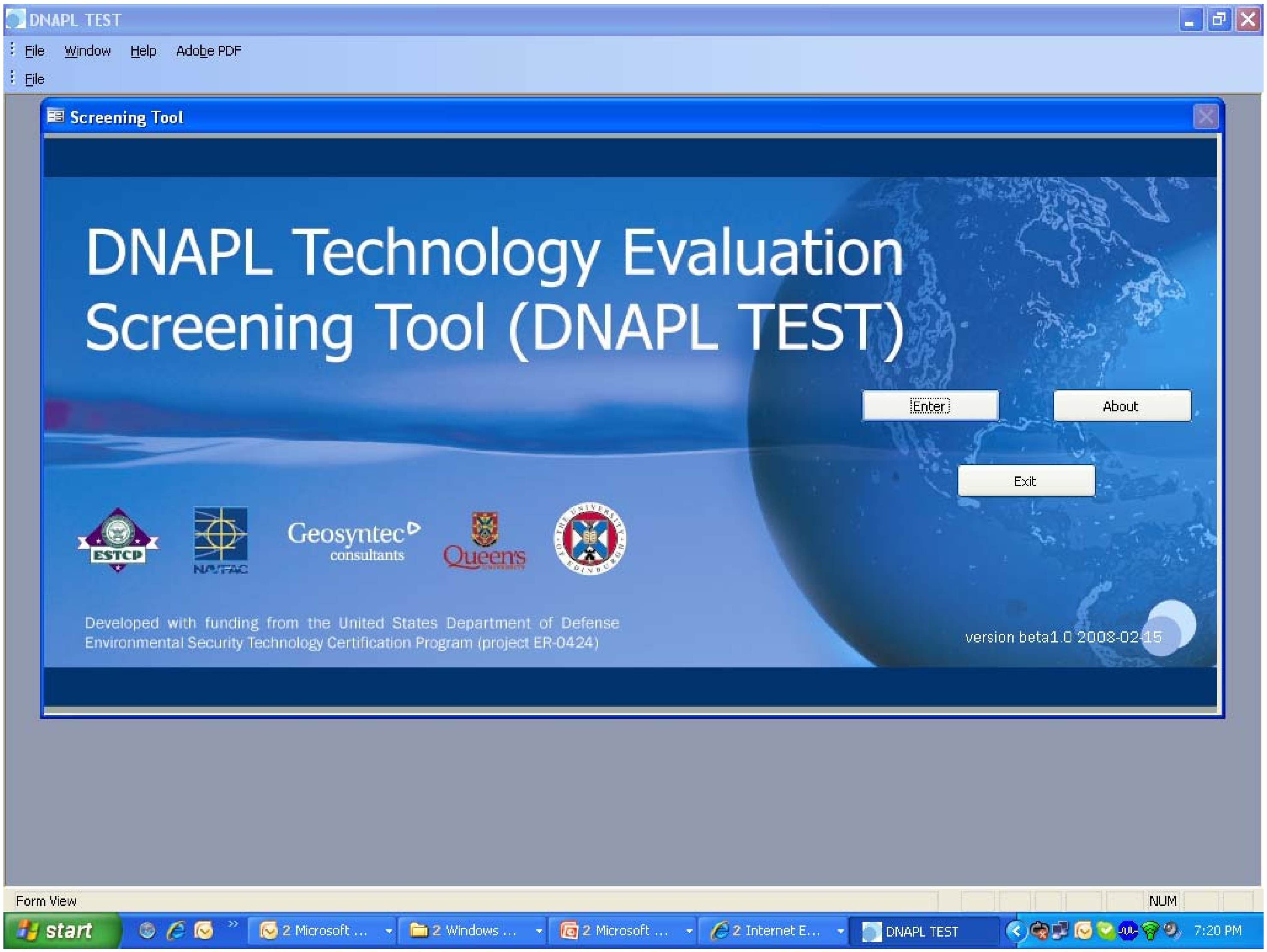
- Thermal typically better at removing DNAPL mass, other technologies more likely to have partial mass removal
- Temporary increases in flux/ concentrations may be seen during EISB due to increased dissolution of the DNAPL and production of more soluble daughter products

Long-Term Impact on Concentrations

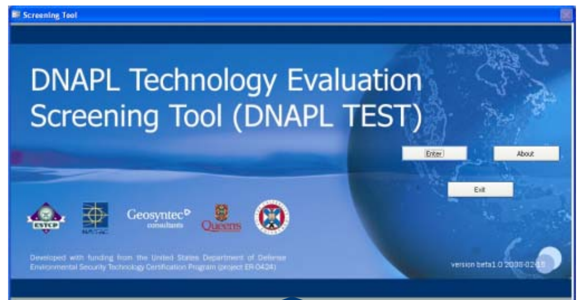


- Extent of mass removal impacts long-term groundwater concentrations
  - Thermal most likely to have near complete mass removal, others more likely to be partial mass removal

Screening Tool Demonstration



Screening Tool Demonstration



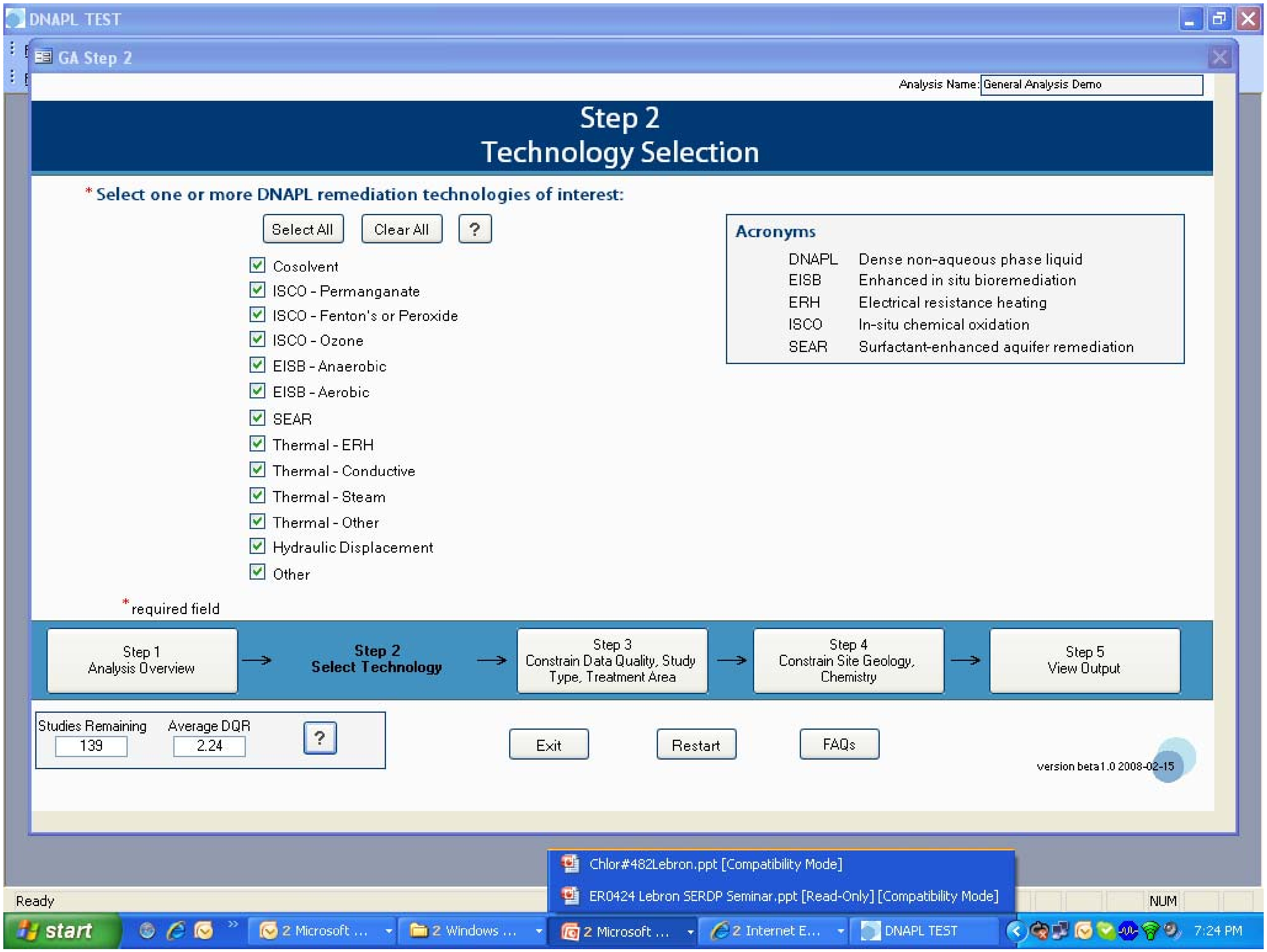
General Analysis

- General trends in tech performance
- Filter out various factors to narrow analysis, evaluate changes

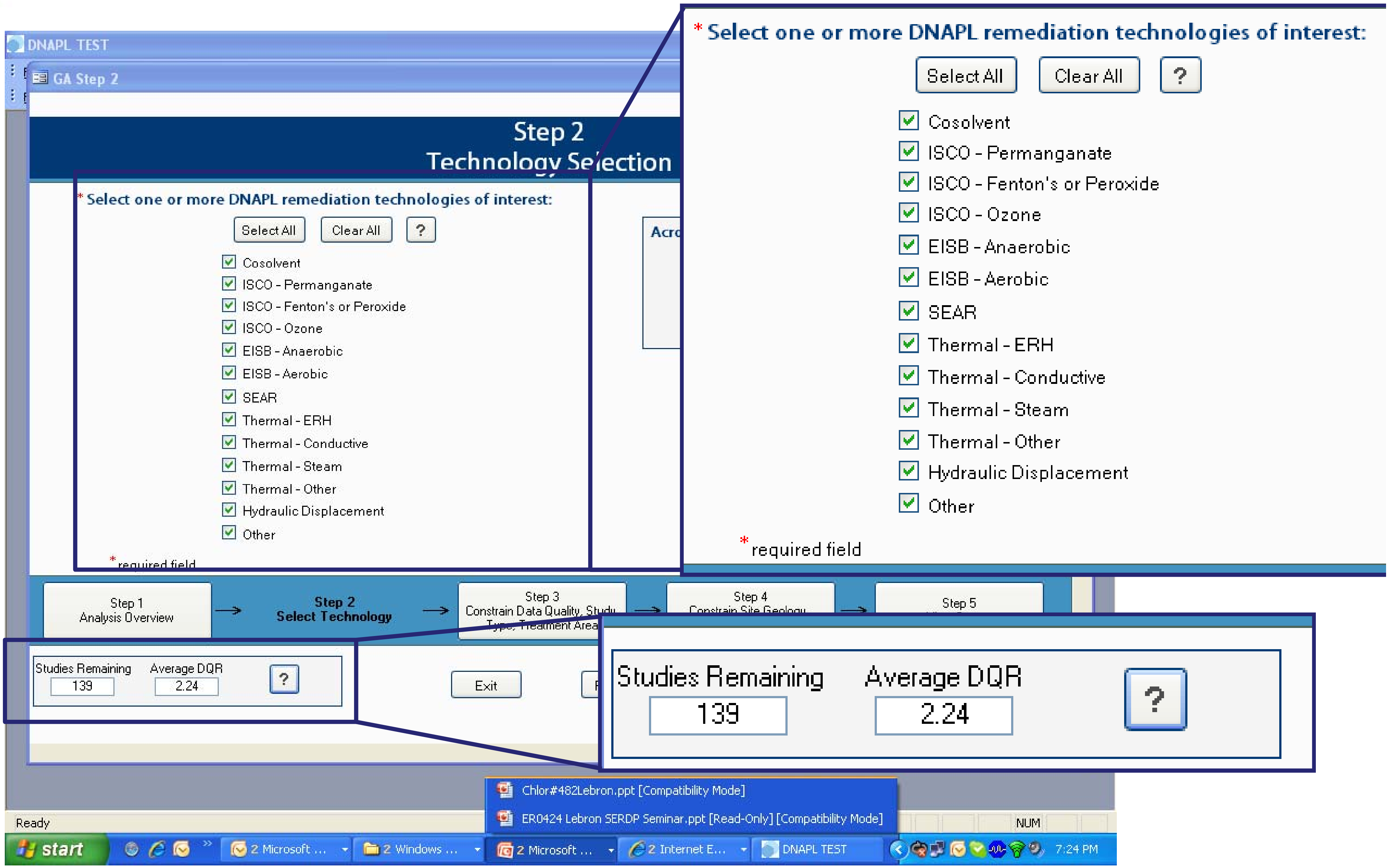
Site-Specific Analysis

- User inputs site parameters of interest
- Tools searches for statistically similar case studies, and outputs technology performance info

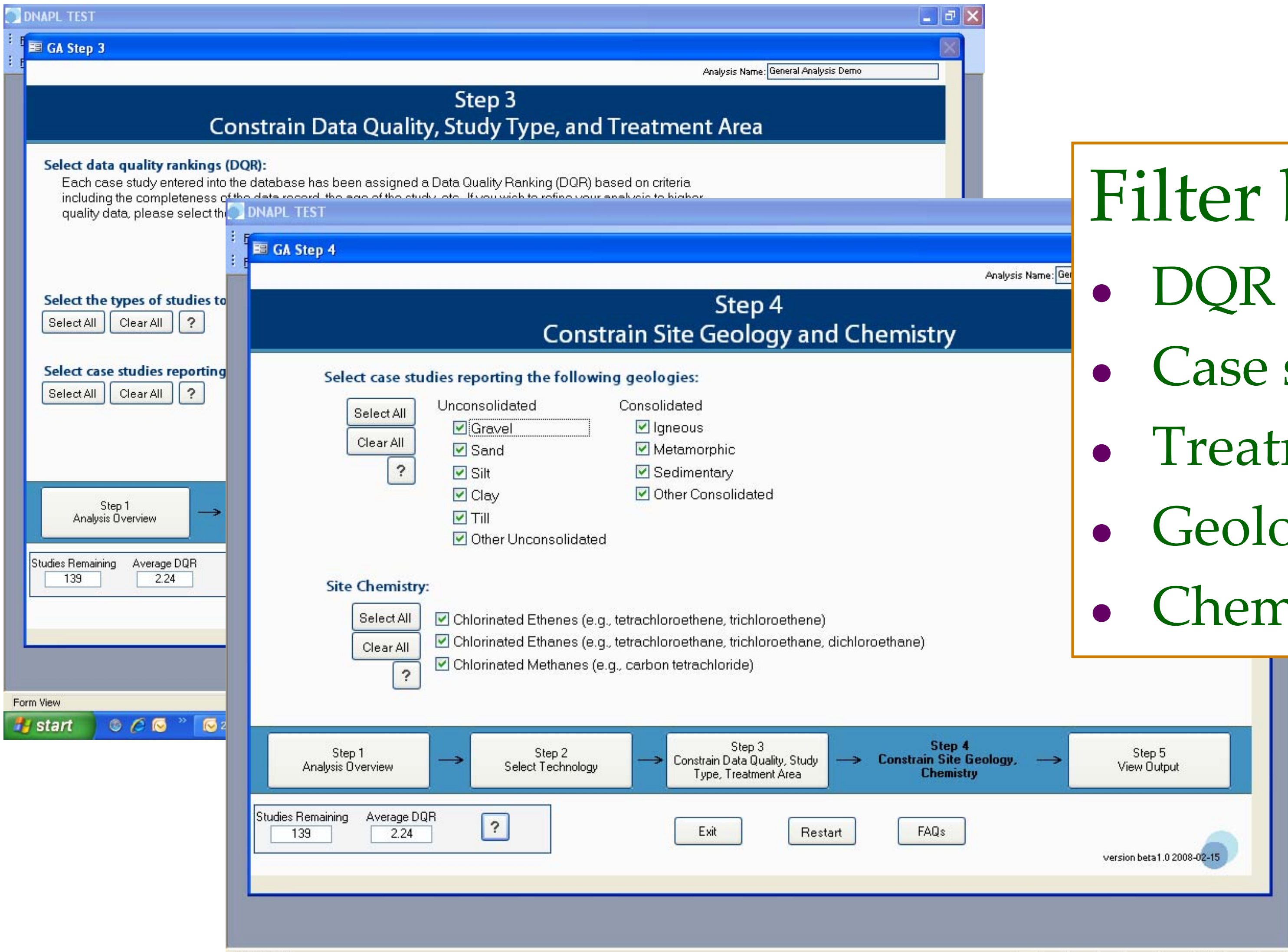
General Analysis Demo



General Analysis Demo



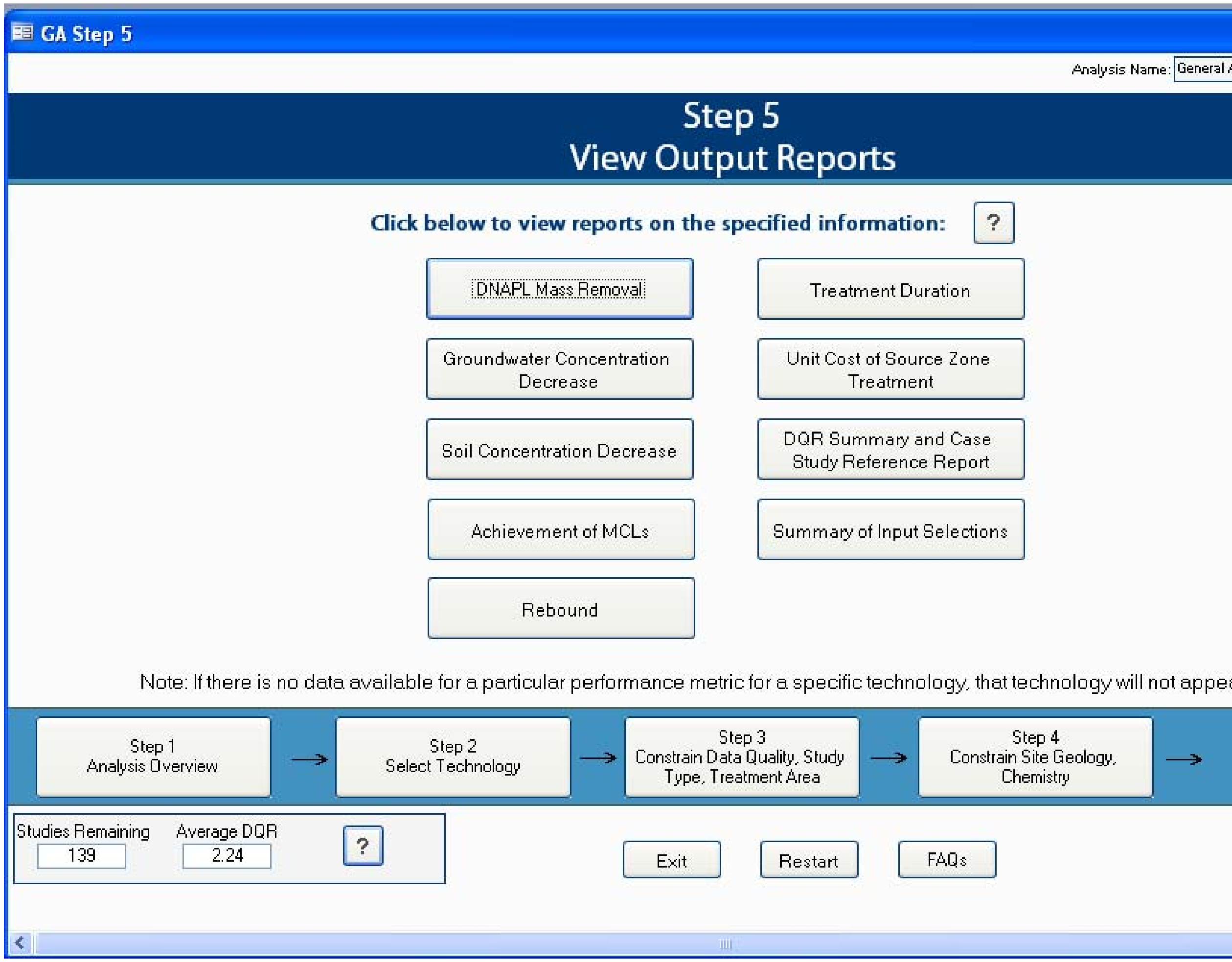
General Analysis Demo

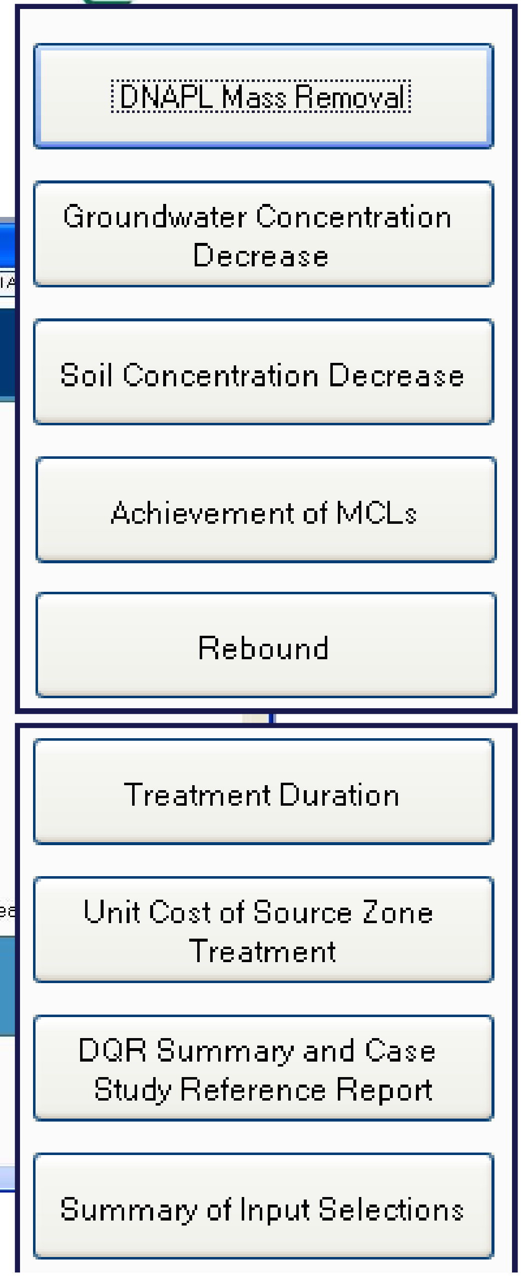


Filter by:

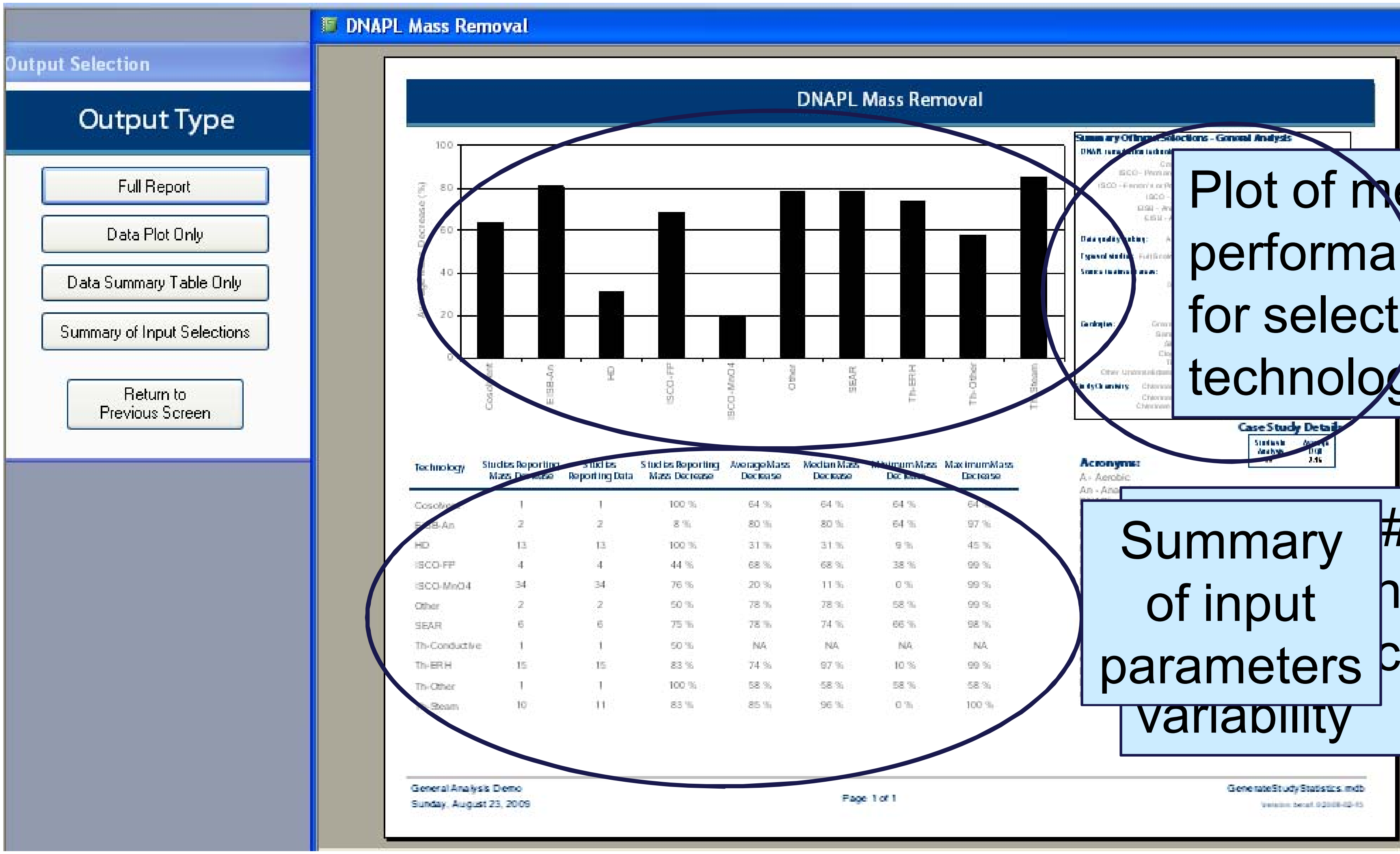
- DQR
- Case study type
- Treatment area
- Geology
- Chemistry

General Analysis Demo





General Analysis Demo



Plot of mean performance for selected technologies

\# n ce, variability

Summary of input parameters

General Analysis Demo

DQR Summary and Case Study Reference
General Analysis Demo

Technology	Case Study Identifier	DQR	Reference Type	Citation
Cosolvent				
	141	2.8		
			Journal	Jawitz JW, Sillan RK, Annable MD, Rao PSC, Warner K. In-Situ Alcohol Flushing of a DNAPL Source Zone at a Dry Cleaner Site. Envirionmental Science and Technology. 2000, 34: 3722-3729.
			Government	IRTC DNAPL Team Case Study Summary Report: Sages Dry Cleaners Jacksonville Florida. www.irtcweb.org/Documents//DNAPLs-3
		1.3		
			Conference	Lewis RF, Dooley MA, Johnson JC, and Murray WA. 1998. Sequential anaerobic/aerobic biodegradation of chlorinated solvents: Pilot-scale field demonstration. In Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, pp. 1-7, vol. C1-6: Physical, Chemical, and Thermal Technologies (Editors: Wickramanayake GB and Hinchee RE), Monterey CA, May 18-21.
EISB-An				
	19	2.1		
			ESTCP	Martin J and Sorenson K. Appendix E.1-Case study of enhanced bioremediation of a DNAPL source area: four years of data from Test Area North, INEEL. In: Principles

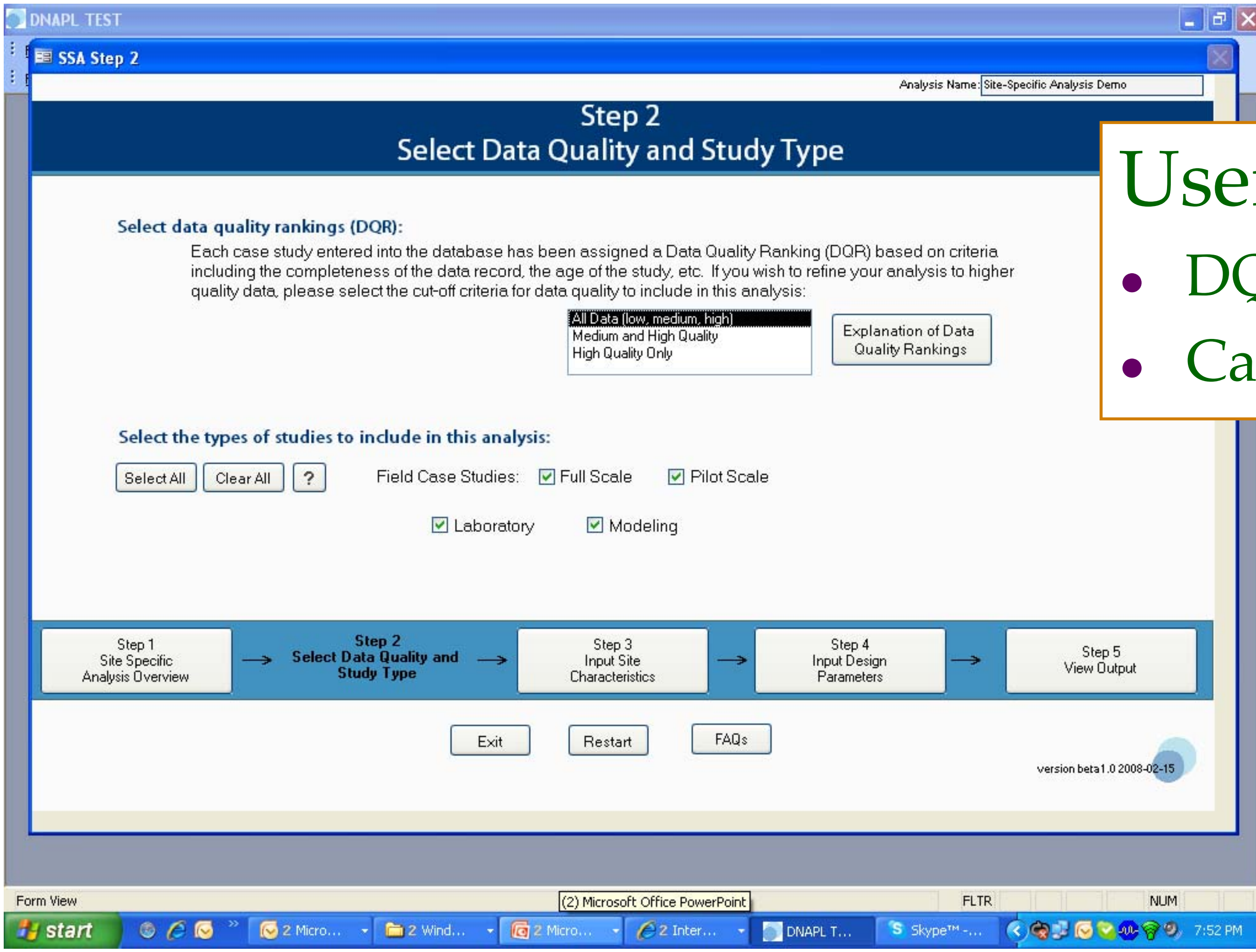
Individual case study reference information

Site-Specific Analysis Demo

- **Demo site characteristics:**
  - **Unconsolidated media, fine to medium-grained sand**
  - **20,000 ft^2 DNAPL source area**
  - **Saturated aquifer thickness of 10 ft**
  - **DNAPL is present as both residual and pools**
  - **Moderate soil heterogeneity (3-5 order of magnitude variability)**

- **Technology of interest – thermal technologies**
  - **Statistically "similar" case studies in database identified by DNAPL TEST using relationships identified as part of the linear and non-linear multi-variate analysis**

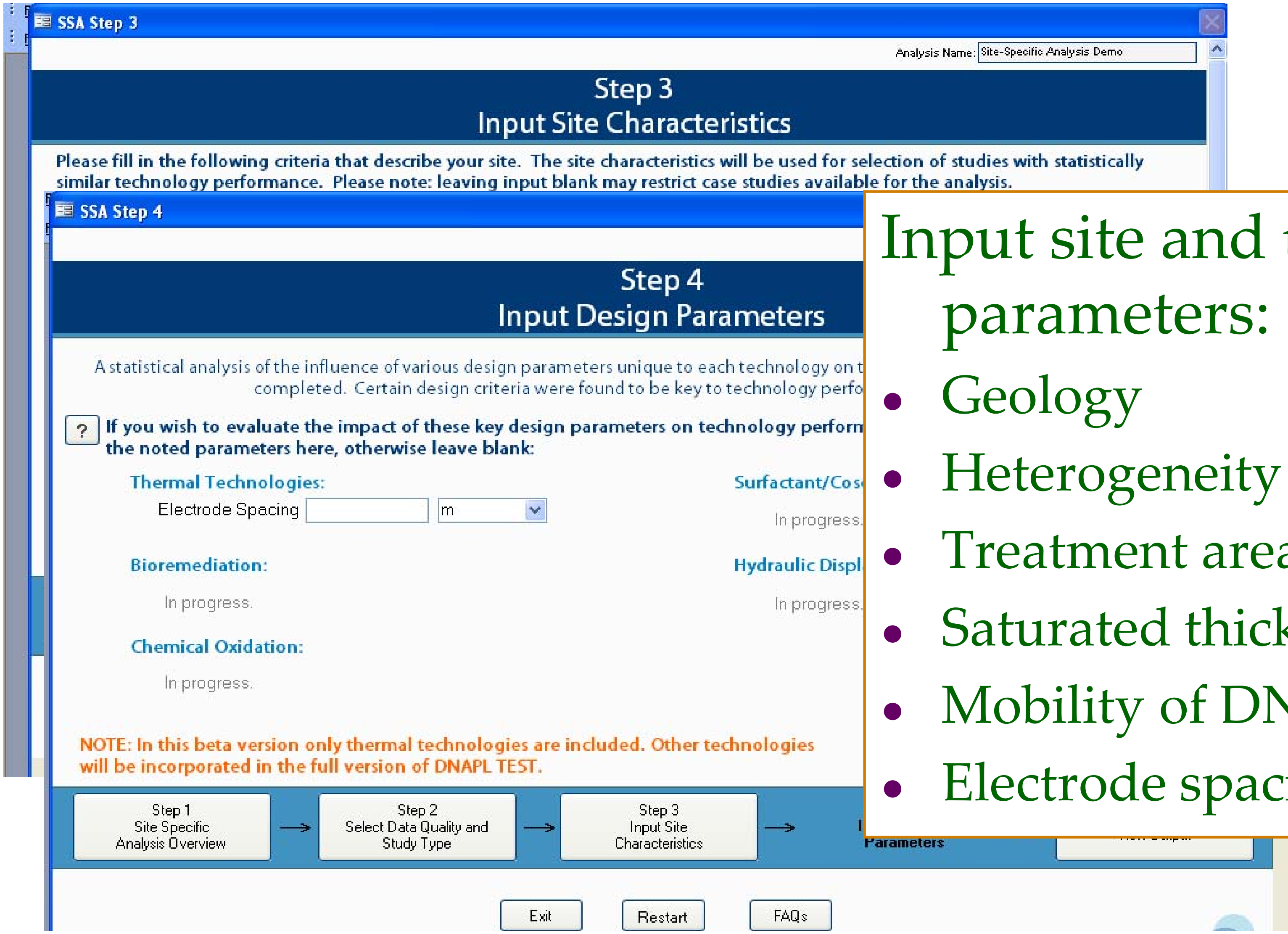
Site-Specific Analysis Demo



User Filters by:

- DQR
- Case study type

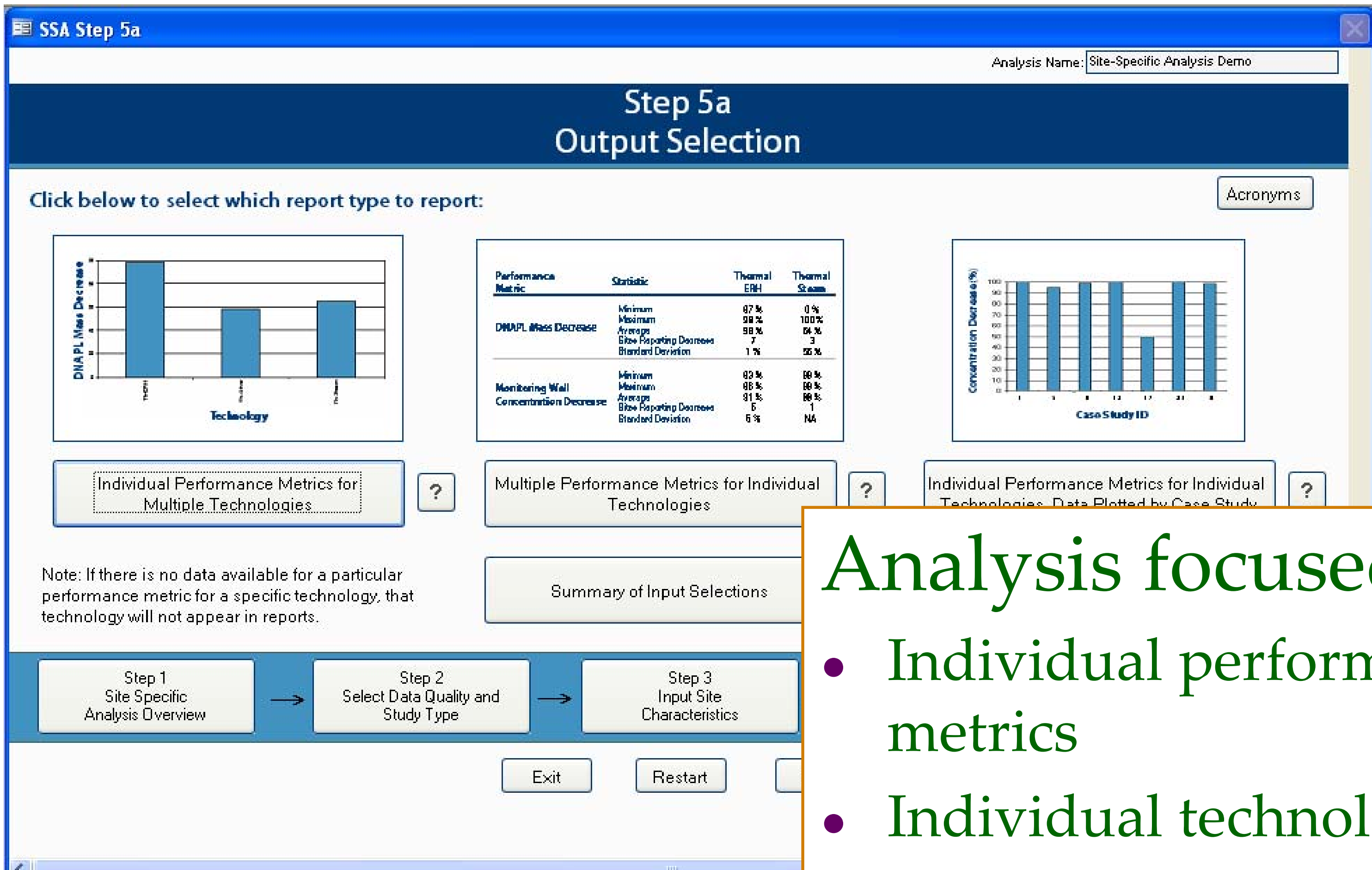
Site-Specific Analysis Demo



Input site and technology parameters:

- Geology
- Heterogeneity
- Treatment area
- Saturated thickness
- Mobility of DNAPL
- Electrode spacing, etc.

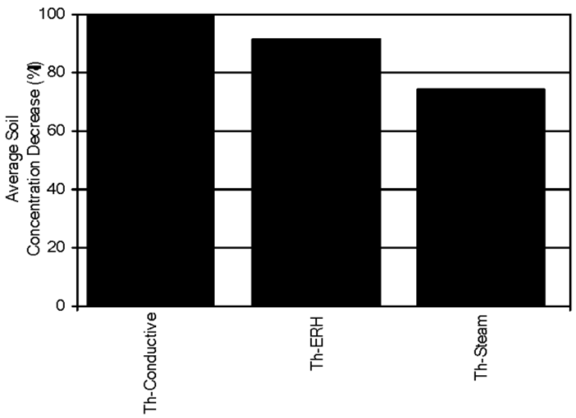
Site-Specific Analysis Demo



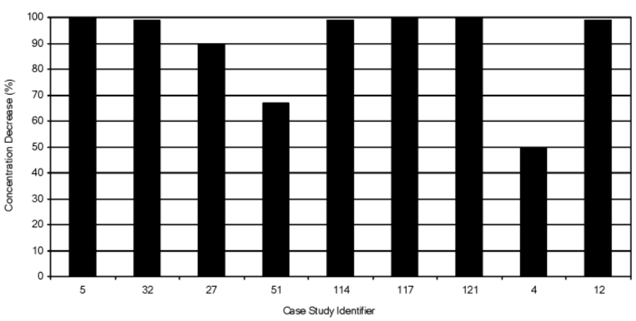
Analysis focused on:

- Individual performance metrics
- Individual technologies, or
- Performance by case study

Site-Specific Analysis Demo



DNAPL Mass Removal	Maximum	90 %	NA	NA
	Average	90 %	NA	NA
	Median	90 %	NA	NA
	Studies Achieving Decrease	3	NA	NA
	Studies Reporting Data	3	NA	NA
	Total Studies	3	NA	NA
Groundwater Concentration Decrease	Minimum	60 %	99 %	NA
	Maximum	99 %	99 %	NA
	Average	87 %	99 %	NA
	Median	91 %	99 %	NA
	Studies Achieving Decrease	10	1	NA
	Studies Reporting Data	10	1	NA
	Total Studies	18	9	NA
Soil Concentration Decrease	Minimum	67 %	50 %	99 %
	Maximum	100 %	99 %	100 %
	Average	91 %	75 %	100 %
	Median	99 %	75 %	100 %
	Studies Achieving Decrease	5	2	2
	Studies Reporting Data	5	2	2
	Total Studies	9	3	2



Performance Metric	Statistic	Thermal ERH	Thermal Steam	Thermal Conductive
DNAPL Mass Removal	Minimum	90 %	NA	NA
	Maximum	90 %	NA	NA
	Average	90 %	NA	NA
	Median	90 %	NA	NA
	Studies Achieving Decrease	3	NA	NA
	Studies Reporting Data	3	NA	NA
	Total Studies	3	NA	NA
Groundwater Concentration Decrease	Minimum	60 %	99 %	NA
	Maximum	99 %	99 %	NA
	Average	87 %	99 %	NA
	Median	91 %	99 %	NA
	Studies Achieving Decrease	10	1	NA
	Studies Reporting Data	10	1	NA
	Total Studies	18	9	NA
Soil Concentration Decrease	Minimum	67 %	50 %	99 %
	Maximum	100 %	99 %	100 %
	Average	91 %	75 %	100 %
	Median	99 %	75 %	100 %
	Studies Achieving Decrease	5	2	2
	Studies Reporting Data	5	2	2
	Total Studies	9	3	2

Summary

- This project has resulted in the creation of one of the most comprehensive database on source treatment technologies
- The modeling has shown to be a powerful means to:
  - Understand what factors affect performance,
  - Allow us to develop case studies for various situations where there are no documented cases, and
  - Increase our knowledge on how these technologies work in different environments
- The tool is infinitely scalable:
  - We can add more data,
  - Run analysis that allows "filtering" of knowledge
    - eg, new information that indicates rind dissolution, which can be modeled
- Screening Tool available by Spring 2010
- Periodic updates as warranted
  - New Case Studies or technologies
  - Enhancements to technologies
  - Continued site monitoring; i.e., Rebound

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

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4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty

Presented by: Ronald Falta (Clemson University)
and Charles Newell (GSI Environmental, Inc.)

ESTCP ER-0704

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- Charles J. Newell and Shahla Farhat, GSI Environmental, Inc.
- P. Suresh Rao and Nandita Basu Purdue University

Model Objectives

Develop a practical analytical tool that allows site managers to:

- Quickly simulate changes in DNAPL source zones and dissolved plumes over time, with and without source remediation, source containment, and/or plume remediation
- Explore site management decisions in a probabilistic framework, so uncertainty becomes an integral part of the decision making process
- Compare the cost, risk, and performance of source treatment to plume treatment approaches

Key Concept: Sources

- Most dissolved plumes can be traced back to a concentrated "source" area, where the original release occurred.
- The source area is usually small compared to the plume footprint
- The source may contain DNAPL, or it may consist of high concentrations of dissolved solvents in low permeability zones
- The **mass of contaminant** in the source zone, and the **mass discharge of contaminant** out of the source zone play a central role in the evolution of dissolved plumes

Key Concept: Plumes

- Plumes are fed by the source, and move with the groundwater flow with some dispersion
- The dissolved contaminants may also adsorb or diffuse into aquifer materials
- The groundwater pore velocity (Darcy velocity divided by porosity) and the rate at which the chemical degrades play a central role the nature of the plume
- High velocities with low decay rates = large plumes
- Low velocities with high decay rates = small plumes

Questions to be addressed by Mass Balance Type Modeling

- What will happen if no action is taken?
- Will source remediation meet site goals? How effective must the source remediation be?
- Will enhanced biodegradation of the plume meet site goals? How effective (and long-lived) must the plume treatment be?
- Should I combine source and plume remediation? How much of each do I need before I get to transition to MNA?
- What is the remediation time-frame?
- What is a reasonable remediation objective?

Core Model: REMChlor

Flow

Source

Analytical model for source behavior

Plume

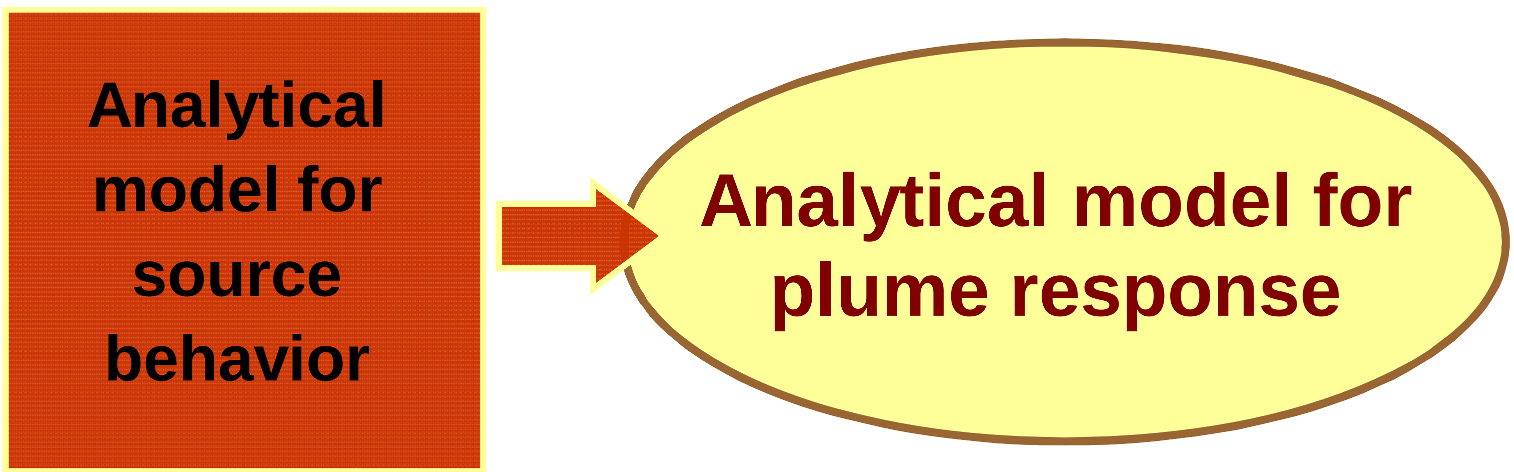
Analytical model for plume response

Mass balance model on source zone predicts discharge <u>including effects of remediation</u>

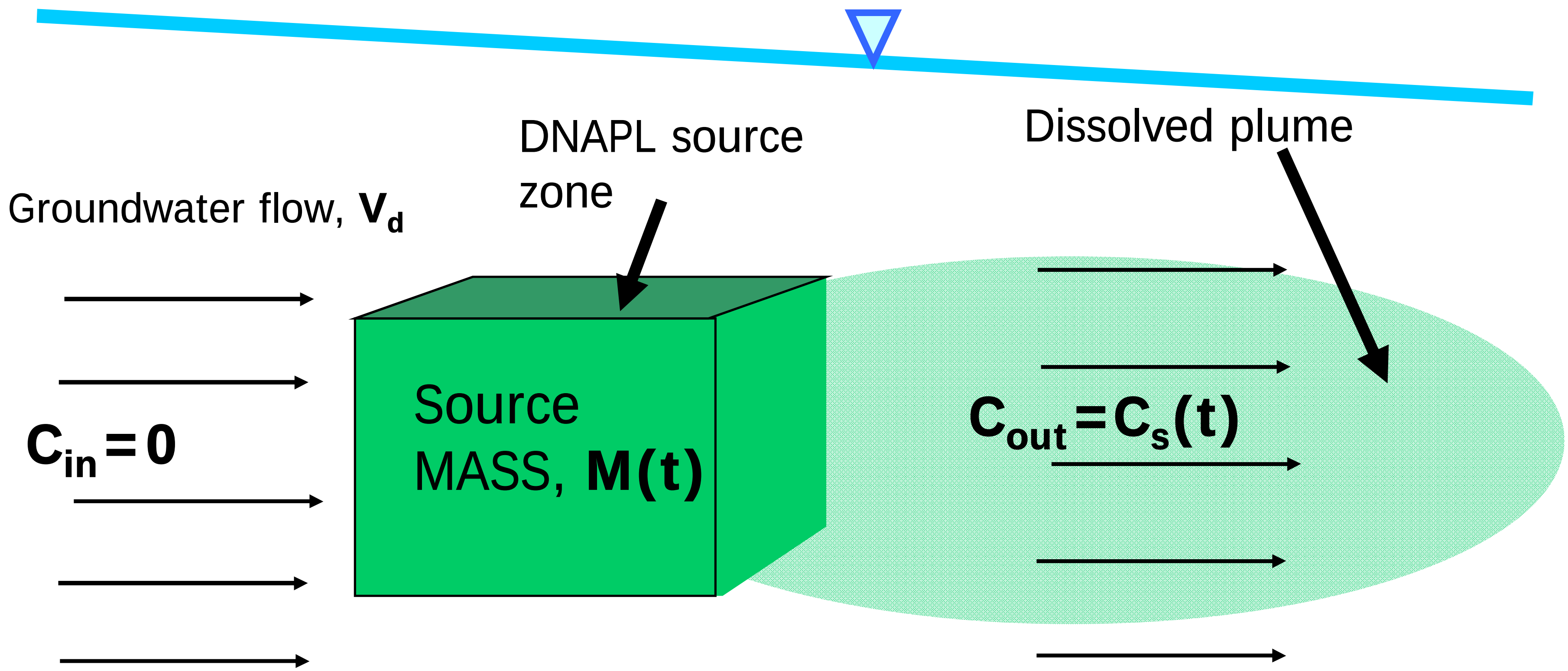
Couple Models At the Edge of the Source Zone to Provide Contaminant Discharge to Plume Model

Plume model simulates mass balance based on advection, dispersion, retardation, and degradation reactions
+
<u>plume remediation</u>
(but all with simple flow field)

Explanation of How the *Source Term* Works in REMCHLOR

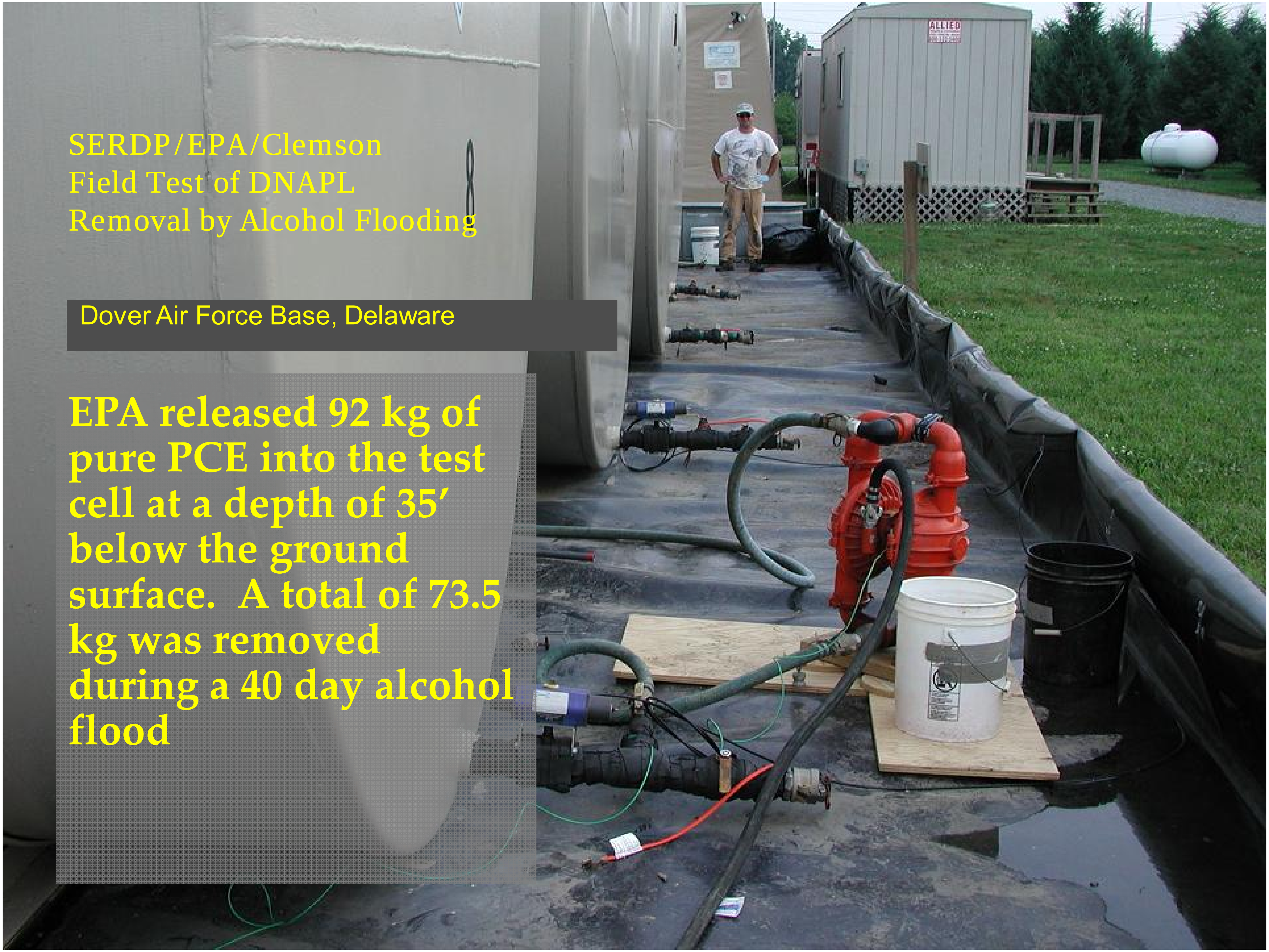


Source conceptual model: Mass is mainly removed by flushing. **The discharging concentration (C_s) depends on the mass remaining in the source zone, (M)**

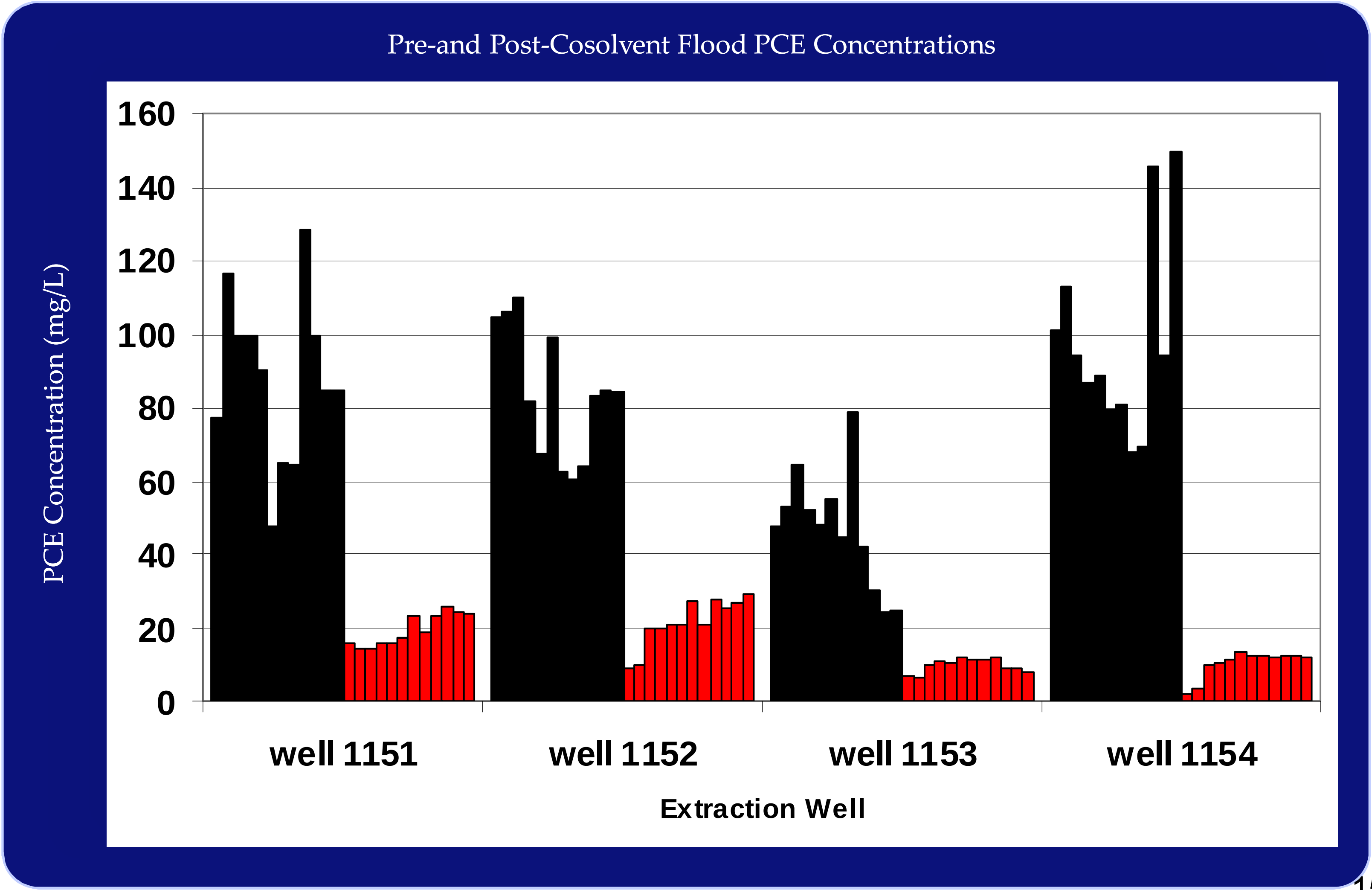


$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M$$

$$\frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^{\Gamma}$$

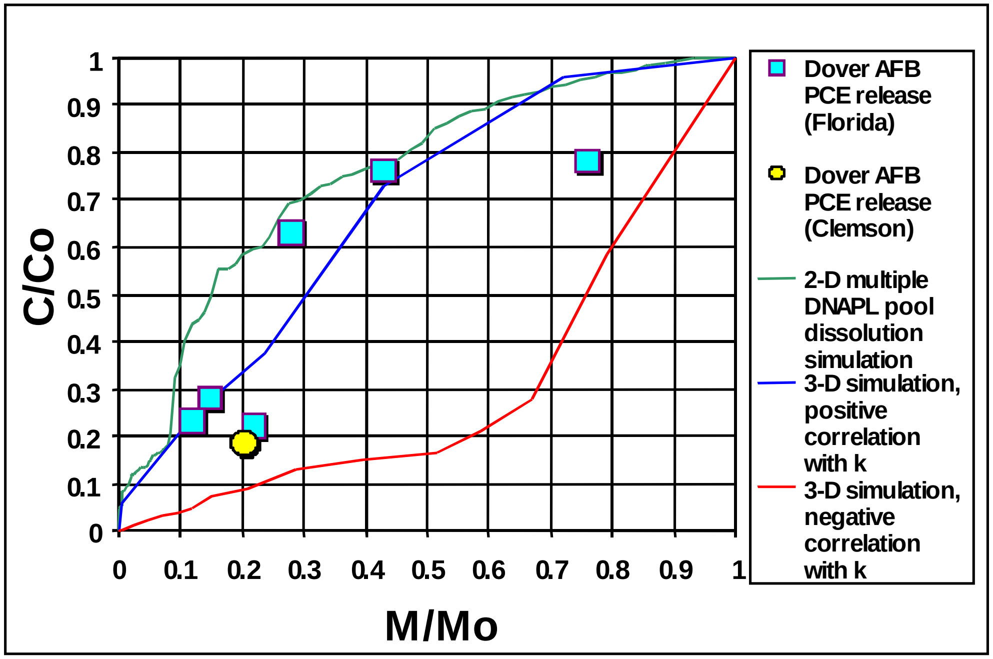

SERDP/EPA/Clemson
Field Test of DNAPL
Removal by Alcohol Flooding
Dover Air Force Base, Delaware
EPA released 92 kg of pure PCE into the test cell at a depth of 35′ below the ground surface. A total of 73.5 kg was removed during a 40 day alcohol flood
ALLIED

80% Source Removal Resulted in 81% Reduction in Groundwater Concentration

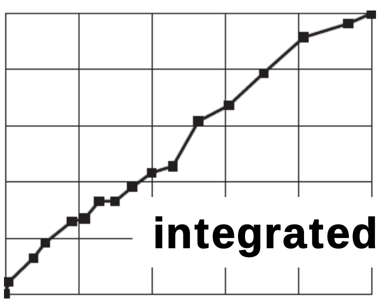


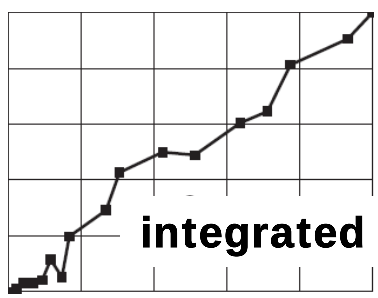
Source Mass Reduction Leads to Discharge Reduction

Field and Modeling Data



Laboratory dissolution experiments



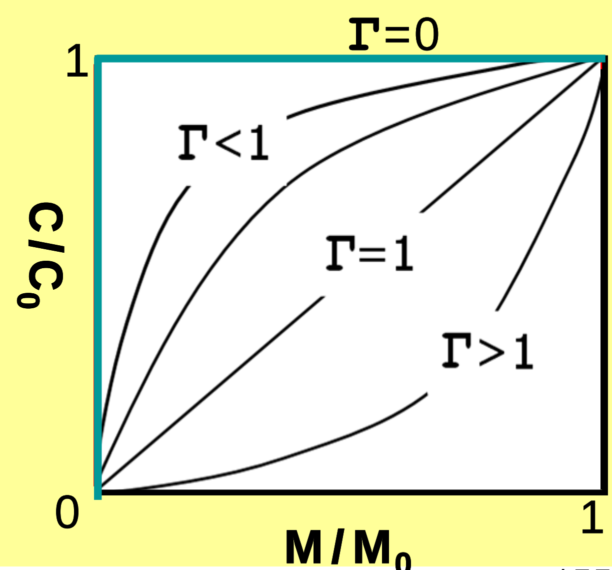


(Jawitz et al.)

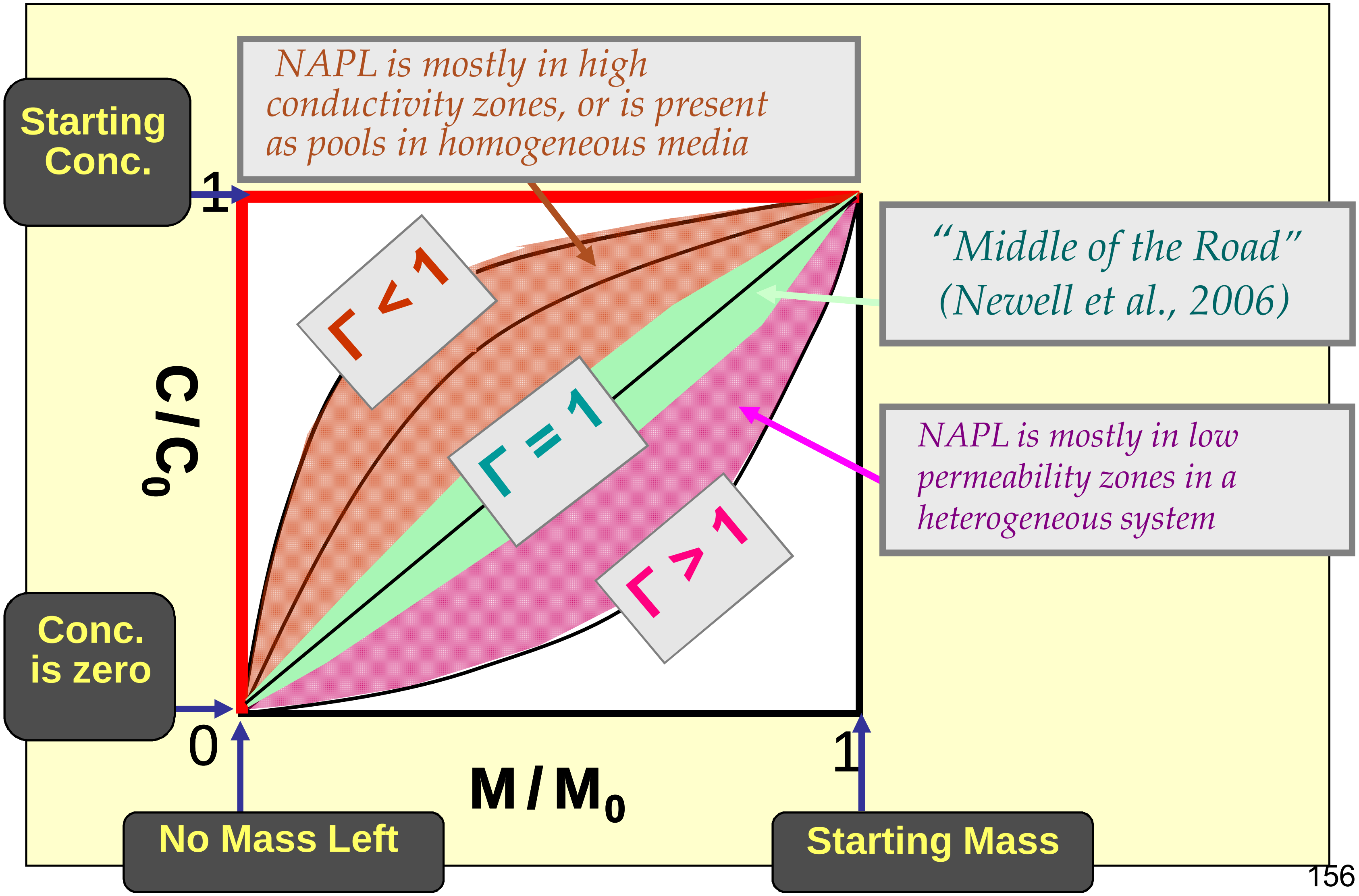
Power function model

[Rao et al., 2001; Parker and Park, 2004; Zhu and Sykes, 2004]

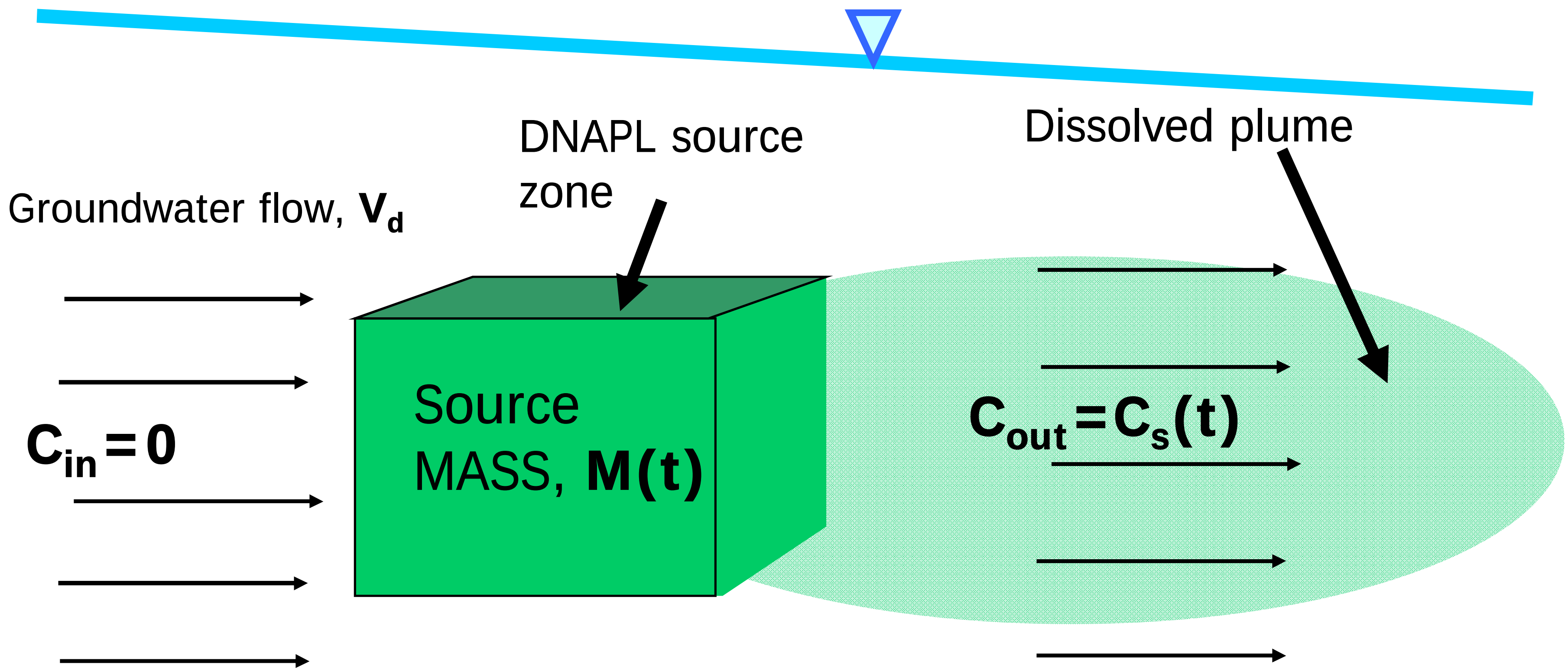
$$\frac{C}{C_0} = \left(\frac{M}{M_0} \right)^{\Gamma}$$



Source Power Function - *What's That?*



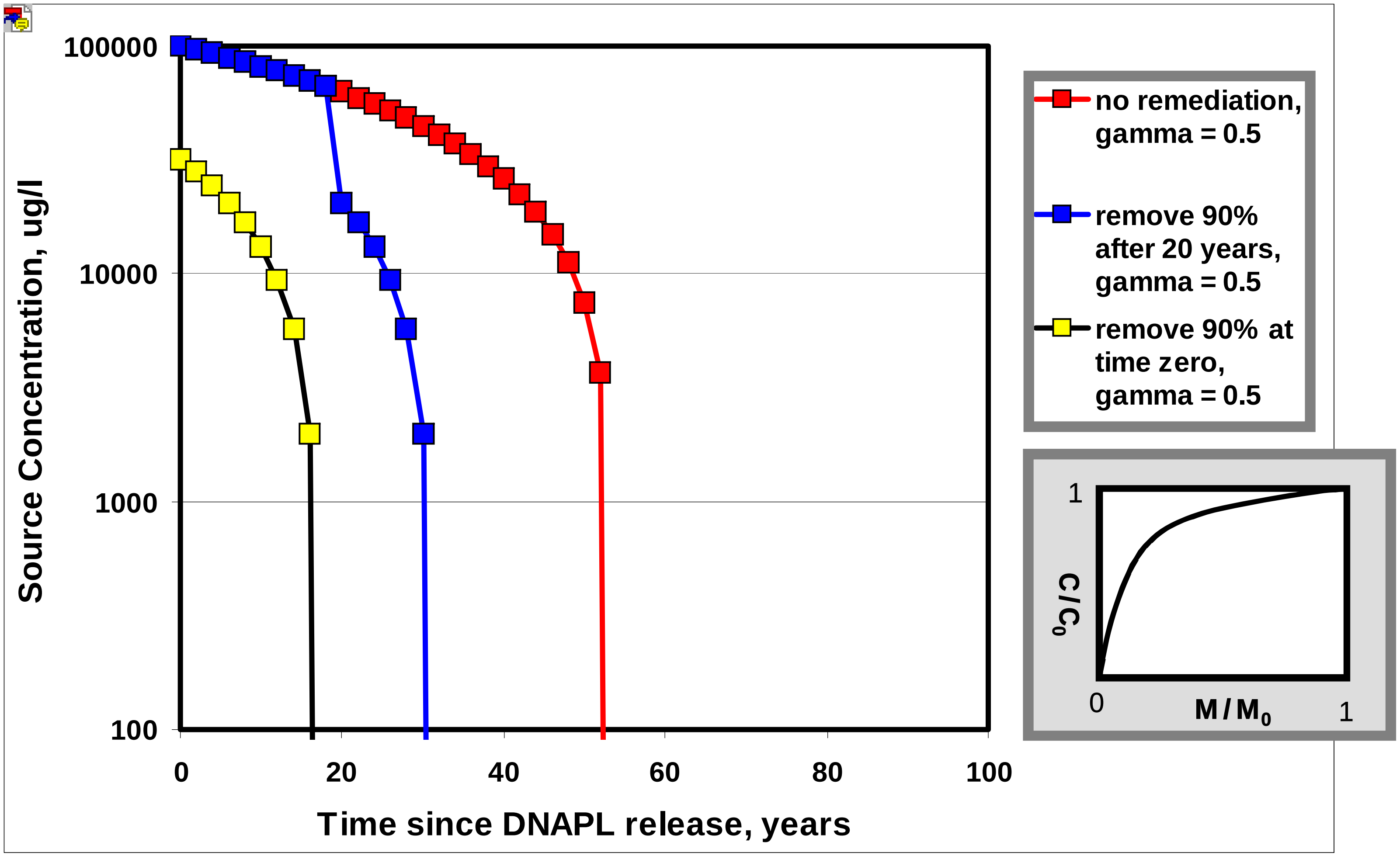
Source conceptual model: Remediation is simulated by removing a fraction of the source mass at the time of remediation



Remove a fraction X of
The mass in source zone
At time TR .

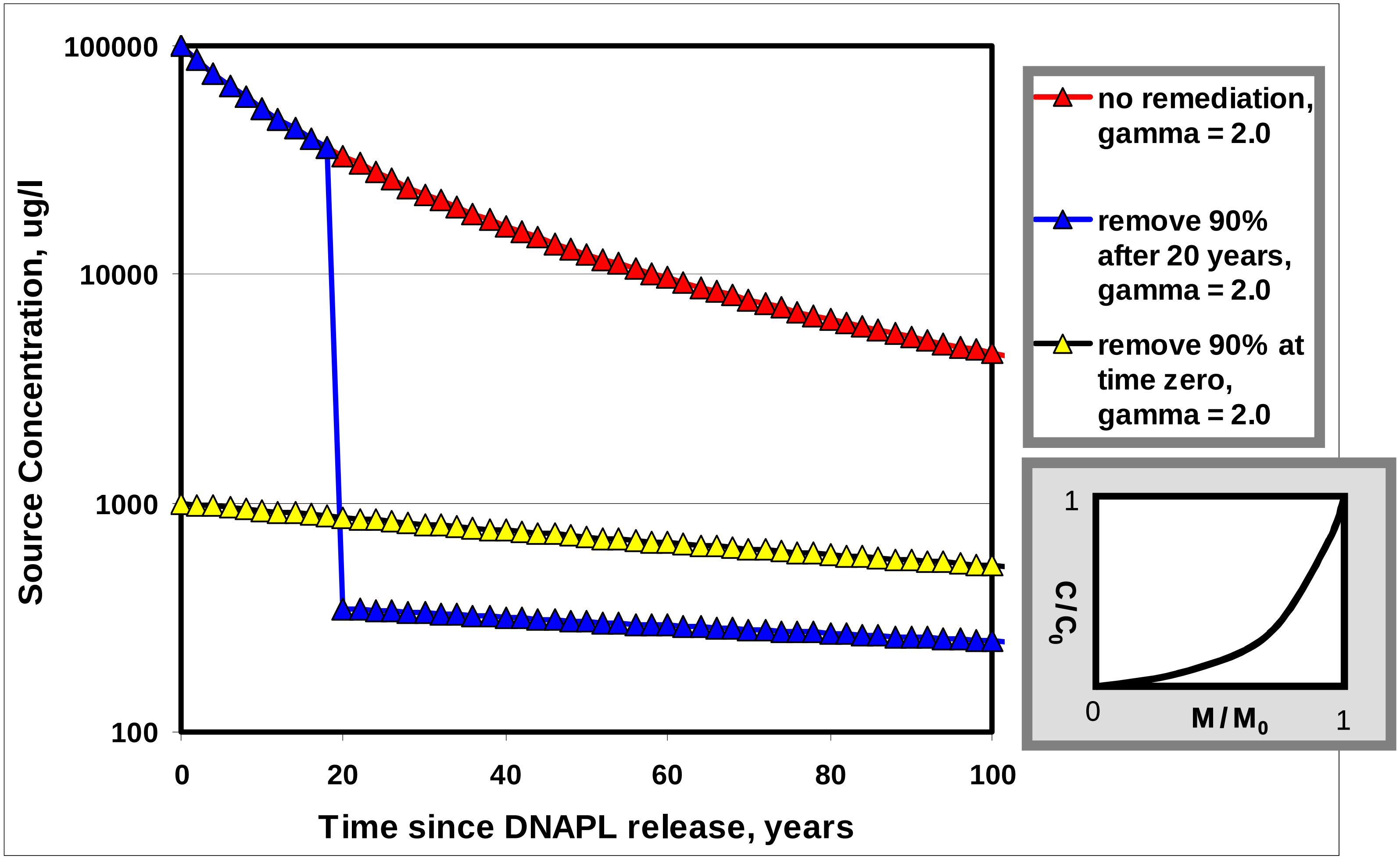
$$C_s = C_0 \left(\frac{(1-X)M_{TR}}{M_0} \right)^{\Gamma}$$

Source Behavior:
$\Gamma = 0.5$, $M_0 = 1{,}620$ kg,
$V = 20$ m/yr, $A = 10$m x 3m, $C_0 = 100$ mg/l



Source Behavior:

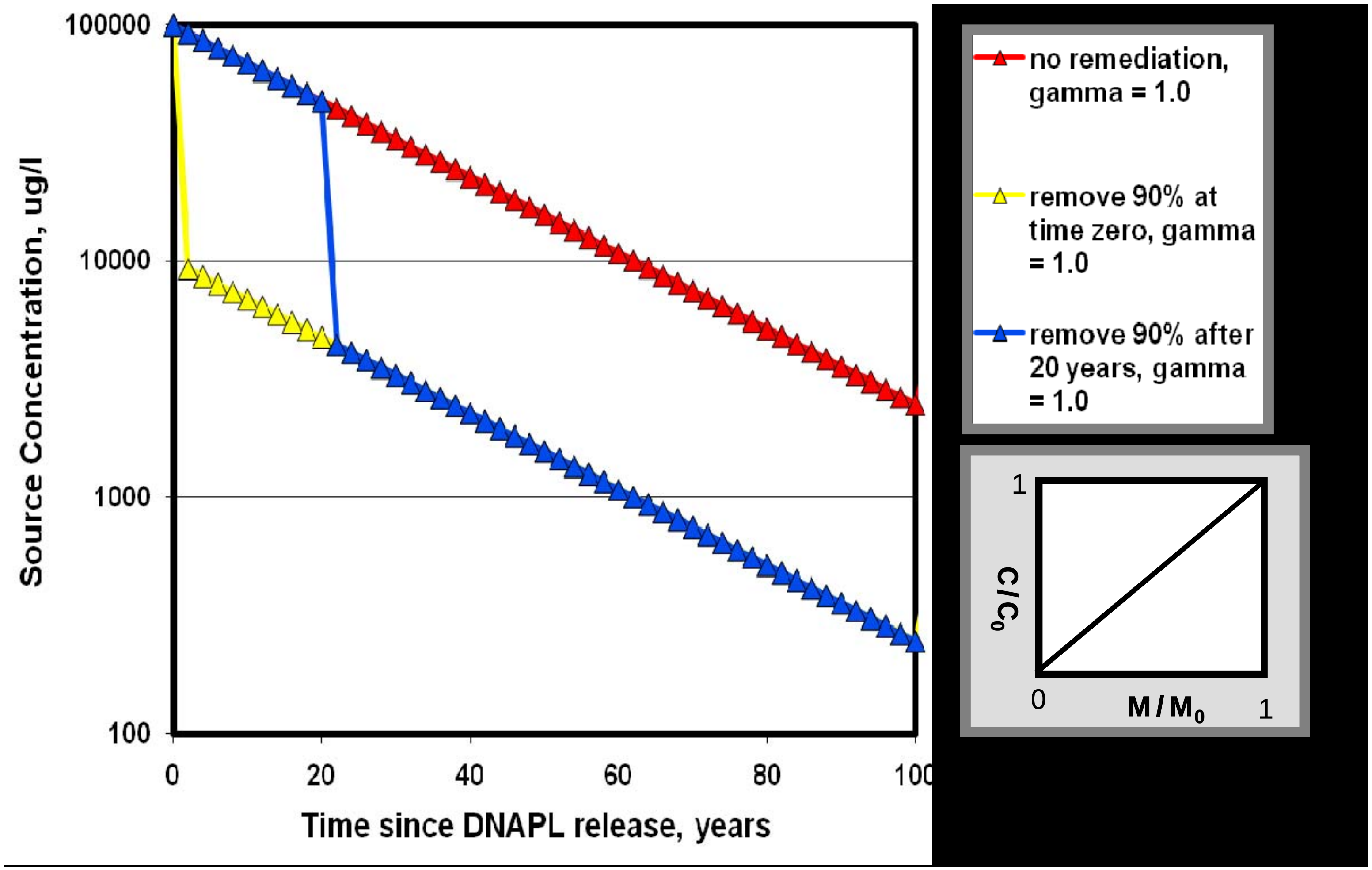
$\Gamma = 2.0$, $M_0 = 1{,}620$ kg,
$V = 20$ m/yr, $A = 10\text{m} \times 3\text{m}$, $C_0 = 100$ mg/l



Source Behavior:

Γ = 1.0, M_0 = 1620 kg,

V = 20 m/yr, A = 10m x 3m, C_0 = 100 mg/l

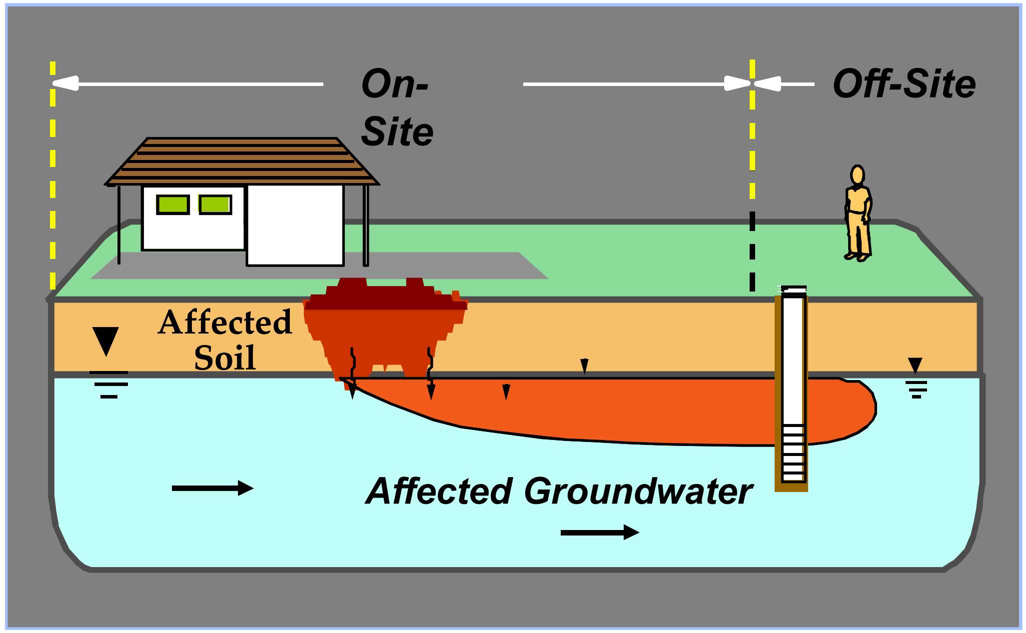


Explanation of How the *Plume* Works in REMCHLOR

Analytical model for source behavior → **Analytical model for plume response**

Key Process in REMChlor

- Source Term
- Advection
- Dispersion
- Adsorption
- **Biodegradation**



Key Mass Balance Equations - *Plume*

Plume equation solved for each species. Equations are linked through the chemical reaction terms

First-Order Decay reactions

$$R\frac{\partial C_i}{\partial t} = -v\frac{\partial C_i}{\partial x} + \alpha_x v\frac{\partial^2 C_i}{\partial x^2} + \alpha_y v\frac{\partial^2 C_i}{\partial y^2} + \alpha_z v\frac{\partial^2 C_i}{\partial z^2} + rxn_i$$

Retardation Coefficient

Longitudinal Dispersivity

Transverse Dispersivity

Vertical Dispersivity

Groundwater Seepage Velocity

Hydraulic Conductivity

Hydraulic Gradient

Effective Soil Porosity

$$V = \frac{K\,i}{n_e}$$

Groundwater Transport Processes - *Biodegradation*

Indigenous micro-organisms are capable of degrading many contaminants.

Need electron donor and electron acceptor.

Fuels **like benzene serve as electron donor.**
Oxygen, nitrate, sulfate, iron are electron acceptor.

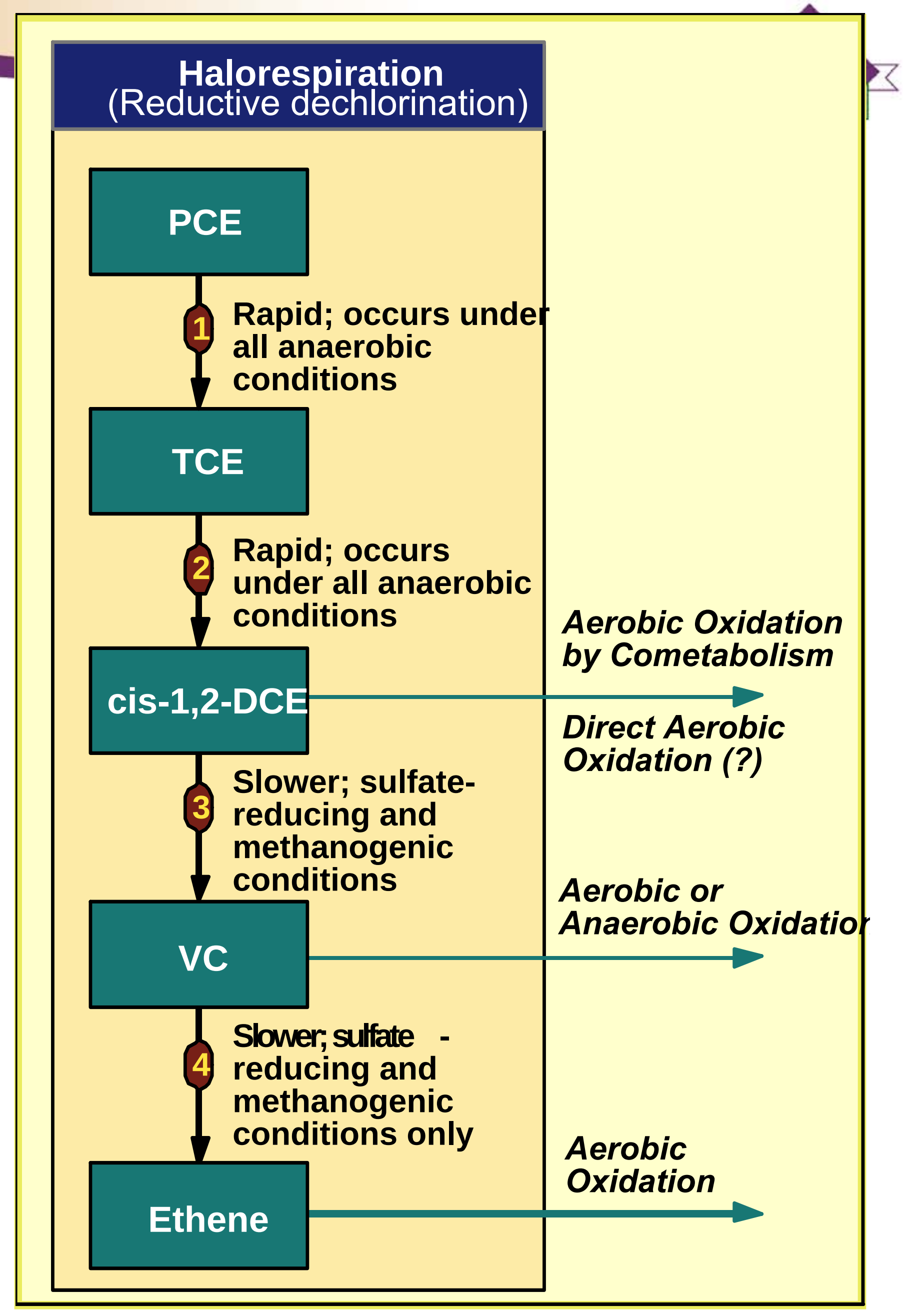
Chlorinated solvents **act as electron acceptor.**
Hydrogen/acetate serve as electron donor.

Biodegradation Decay Chain for Chlorinated Ethenes

Key footprints

cis-DCE

ethene or ethane



(Adapted from RTDF, 1997)

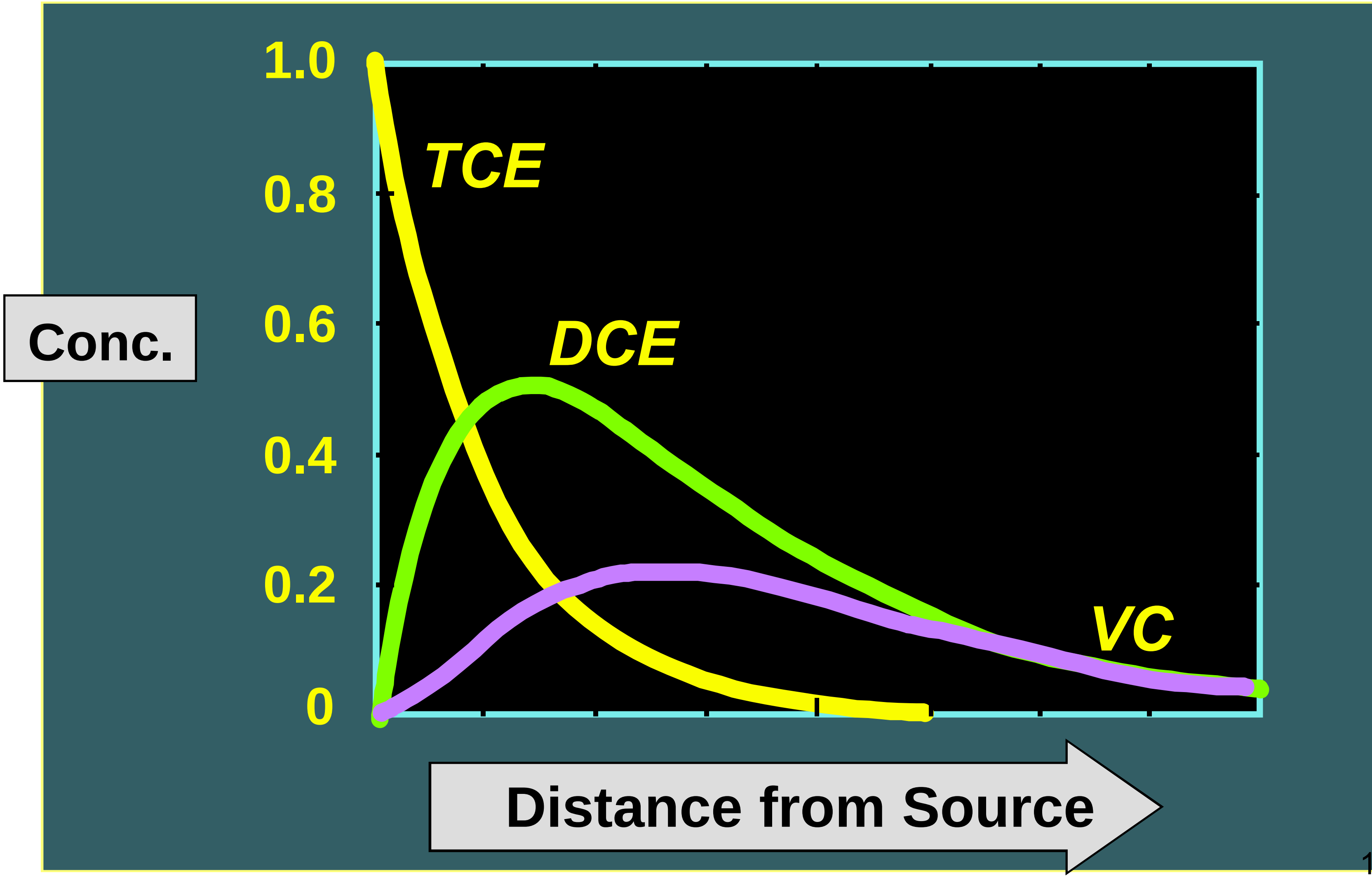
Sequential Reactions

$$PCE \xrightarrow{\lambda_1} TCE \xrightarrow{\lambda_2} DCE \xrightarrow{\lambda_3} VC \xrightarrow{\lambda_4} ETH$$

$$Rate_{PCE} = -\lambda_1 C_{PCE}$$

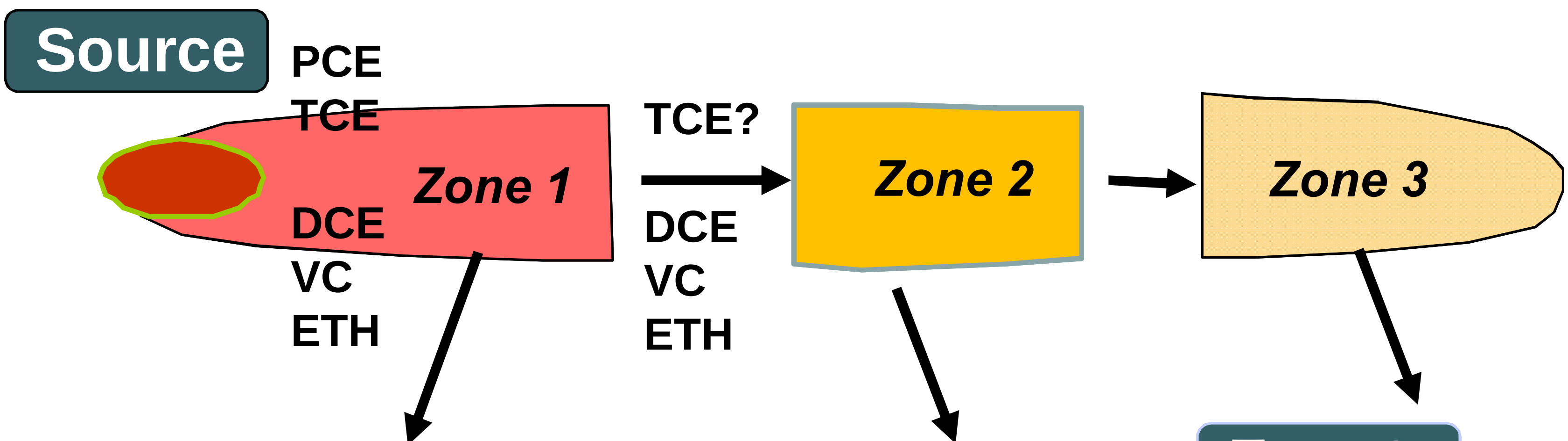
$$Rate_{TCE} = \lambda_1 y_1 C_{PCE} - \lambda_2 C_{TCE}$$

Results of Sequential Reactions



REMChlor Model: Other Features

Three Reaction Zones for Mixed Sites



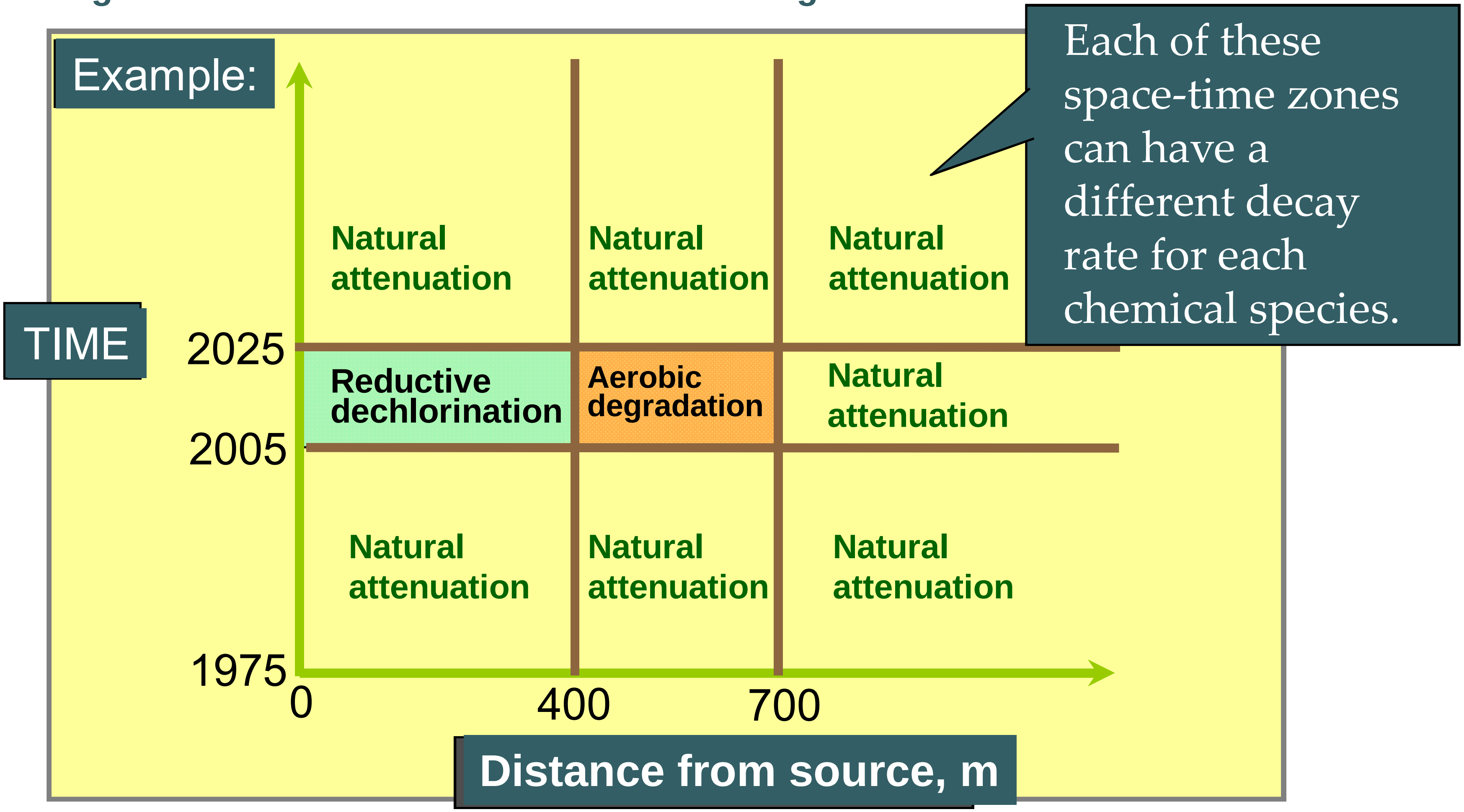
Zone 1:
High Anaerobic Decay Rates
(Carbon Present)

Zone 2:
Possible Enhanced Aerobic Decay

Zone 3:
Low or Background Decay Rates

Plume Remediation Model

Divide space and time into "reaction zones", solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone

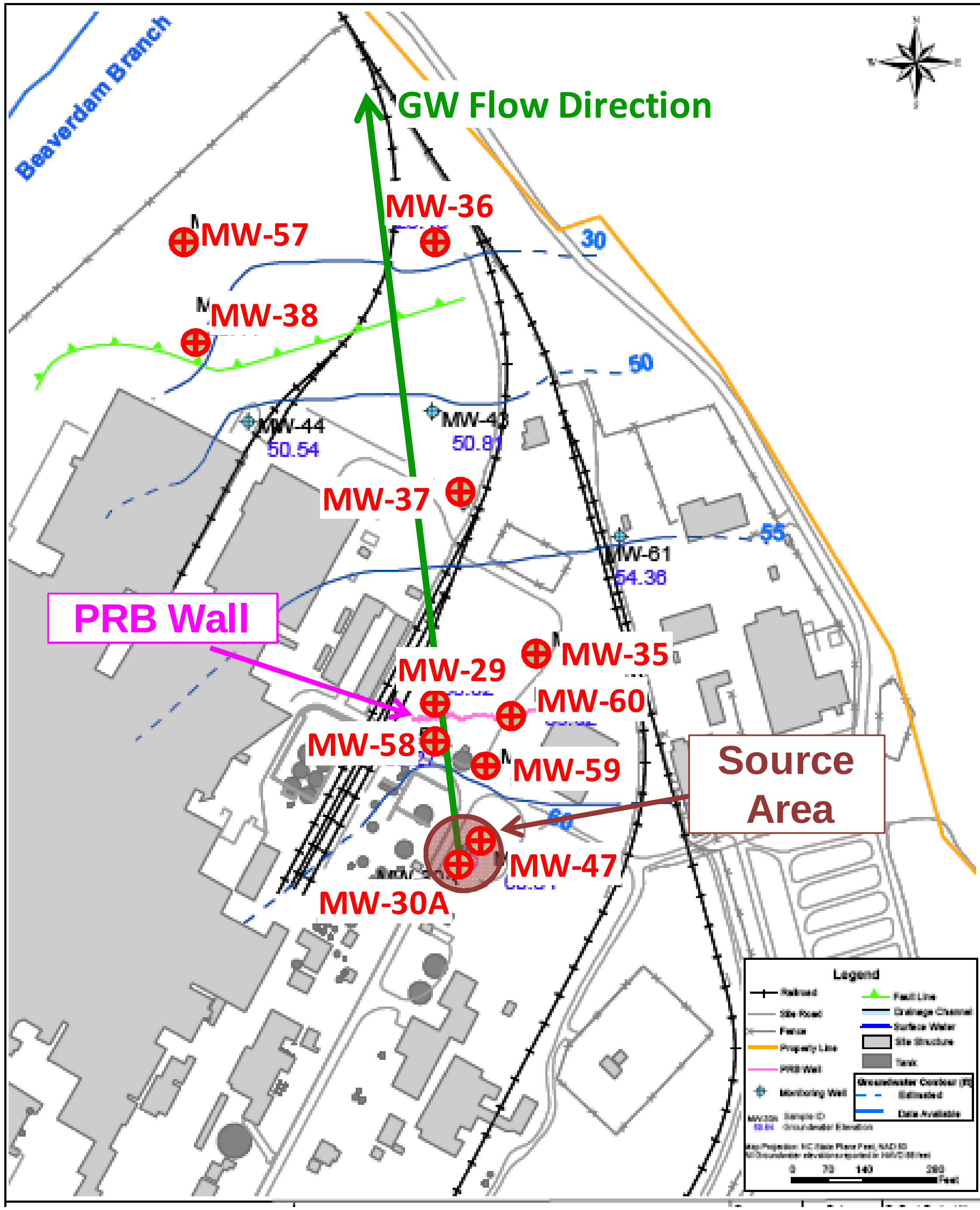


REMChlor Case Study: TCE plume at a manufacturing plant in North Carolina

- DuPont Kinston Plant in eastern NC, currently produces Dacron polyester resin and fibers
- TCE contamination of groundwater discovered in the late 1980's; ~ stable plume about 1250 ft long (380 m).
- Release date unknown, but before 1980.
- Plume is dominated by TCE; small amounts of cis-1,2-DCE are present and VC is essentially absent
- Groundwater velocity is slow, less than 100 ft/yr pore velocity

REMChlor Case Study: TCE plume at a manufacturing plant in North Carolina

- Source zone TCE mass estimated at 300 lbs (136 kg), source zone concentrations up to ~6,000 ug/l
- Source remediation took place in 1999, consisting of ZVI injection throughout the suspected source zone. Although source mass removal was reported as 95%, wells in the source zone have not seen large reductions in concentration.
- A 5 inch thick permeable reactive barrier (PRB) using ZVI was installed 290 ft downgradient of the source in 1999.

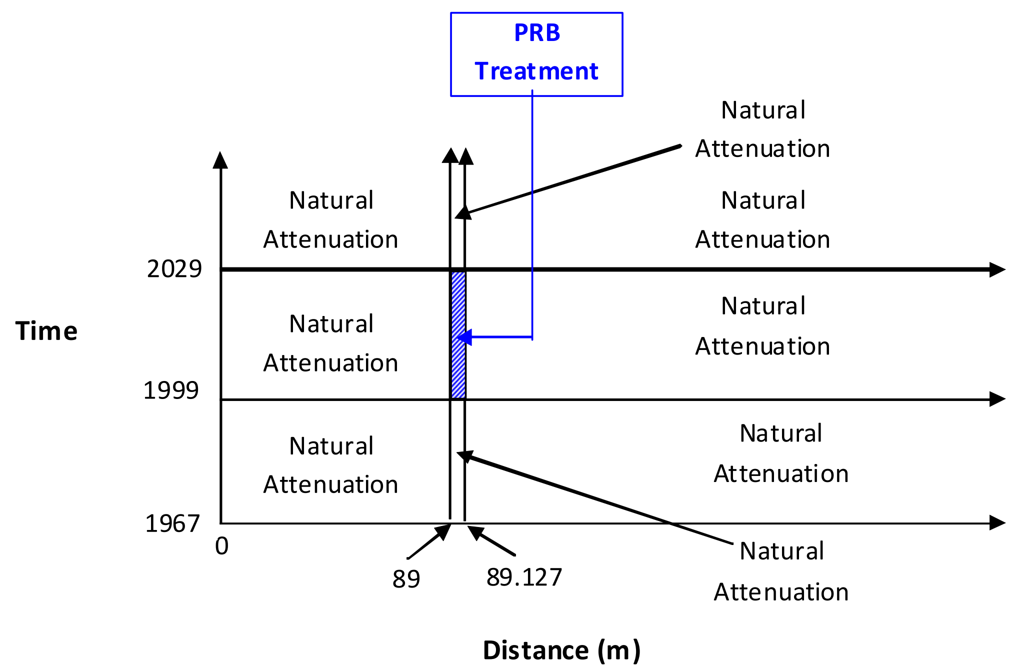

Beaverdam Branch
GW Flow Direction
MW-36
MW-57
MW-38
30
50
MW-44
50.54
MW-43
50.81
MW-37
55
MW-61
54.38
PRB Wall
MW-35
MW-29
MW-60
MW-58
MW-59
60
Source Area
MW-47
MW-30A
Legend
Railroad
Site Road
Fence
Property Line
PRB Wall
Monitoring Well
Fault Line
Drainage Channel
Surface Water
Site Structure
Tank
Groundwater Contour (ft)
Estimated
Data Available

REMChlor Model Parameters for Transport/Natural Attenuation

Parameter	Value	Comment
Initial Source Conc., C_o	6,000 ug/l	Estimated from source wells
Initial Source Mass, M_o	136 kg	From site reports; assume 1967 release date
Source function exponent, Γ	1	Estimated
Source Width, W	8m	From site reports
Source Depth, D	3.5m	From site reports
Darcy velocity, V	8m/yr	Calibrated; reports had estimated 1.5 to 4.6 m/yr
Porosity, φ	0.33	From site reports
Retardation Factor, R	2	Estimated
Longitudinal dispersivity, α_l	x/20	Calibrated
Transverse dispersivity, α_t	x/50	Calibrated
Vertical dispersivity, α_v	x/1000	Estimated
TCE decay rate in plume, λ	0.125/yr	Calibrated (equal to $t_{1/2}$ of 5.5 yrs)

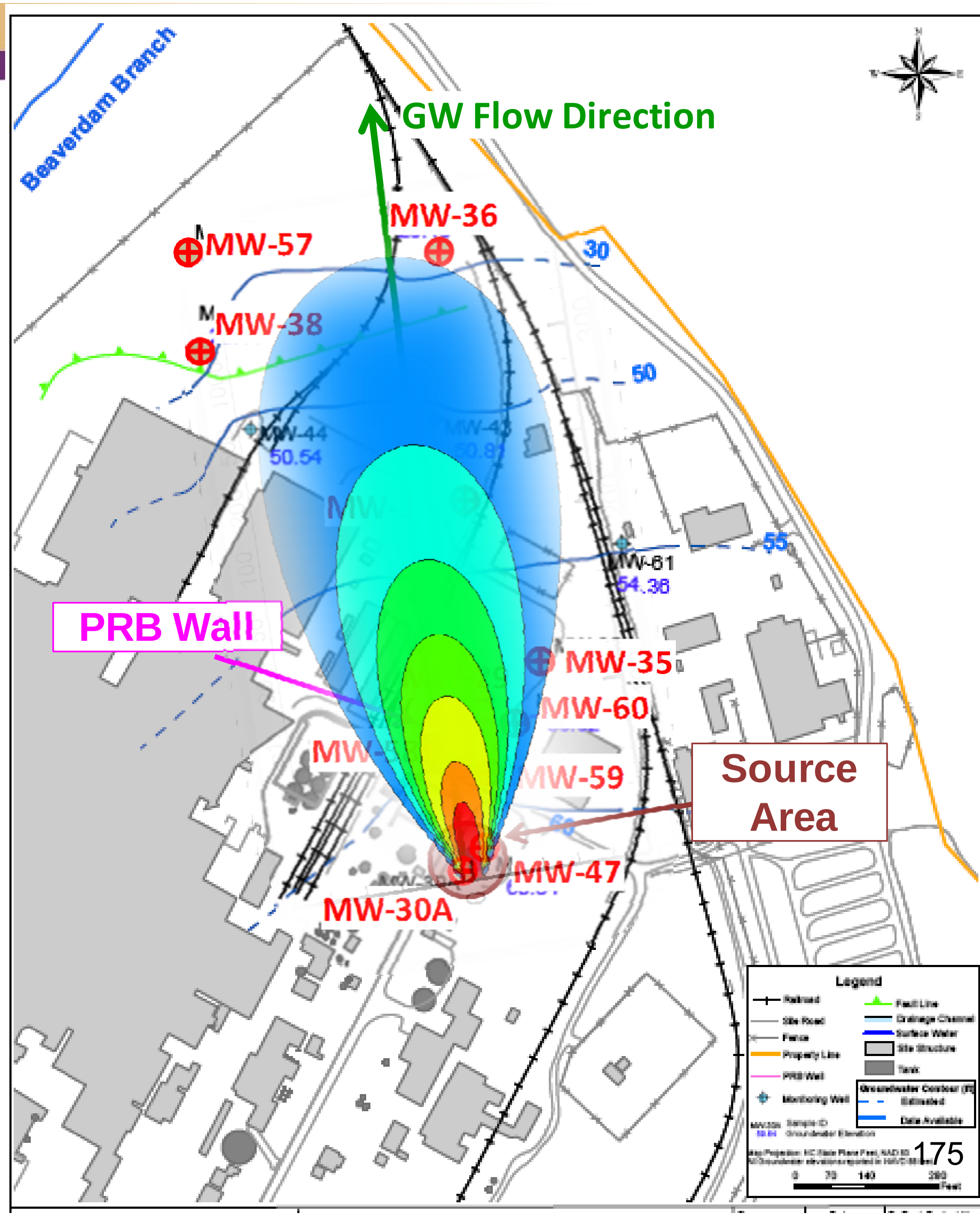
REMChlor Model Parameters for Source and Plume Remediaton

Parameter	Value	Comment
Fraction of source removed in 1999, X	95%	From site reports (but large uncertainty)
PRB wall thickness (after 1999)	0.127m (5")	From site reports
TCE decay rate in PRB	435/yr	Estimated from well data (equal to $t_{1/2}$ of 14 hours)



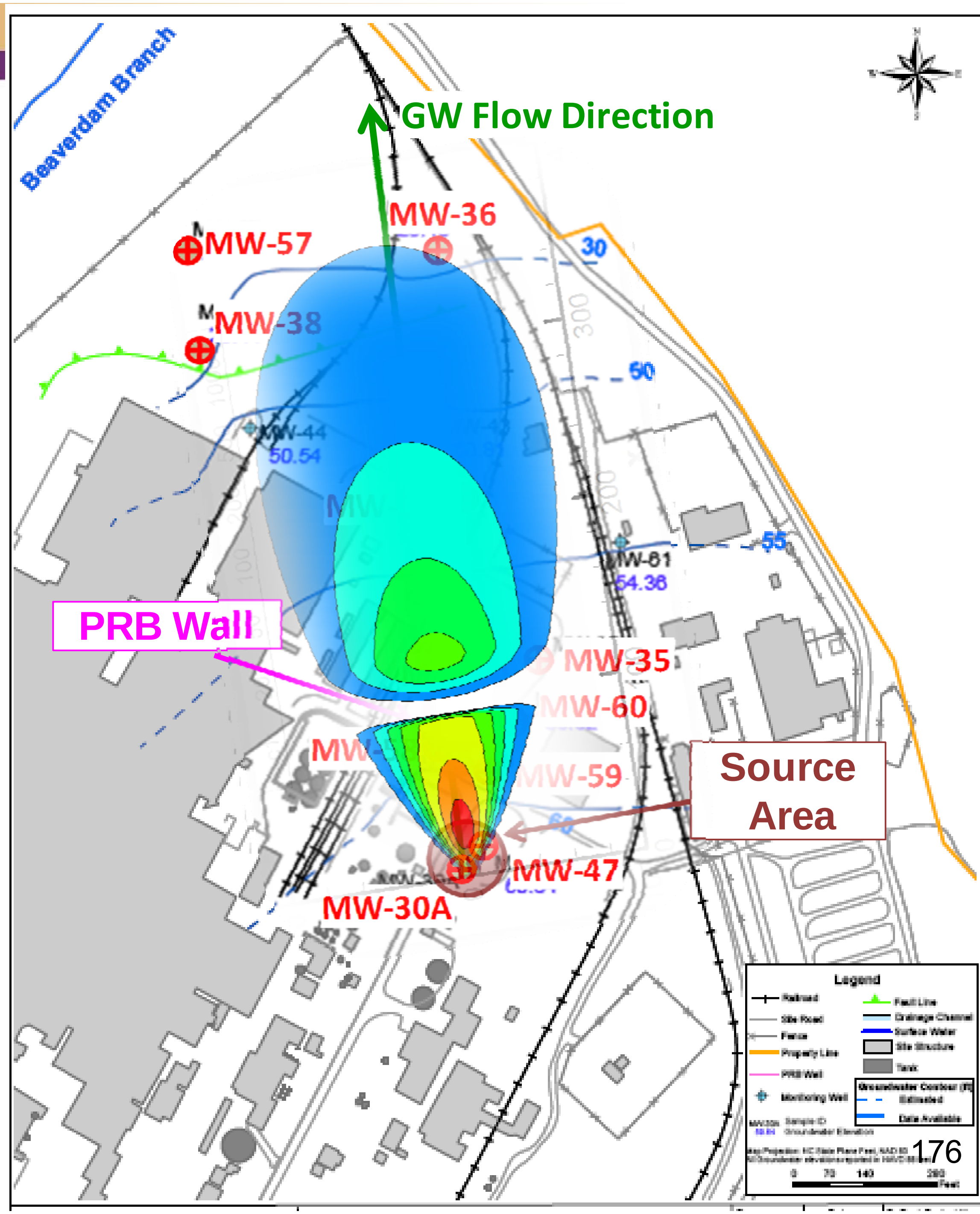
Simulated TCE concentrations In 1999 prior to source remediation or PRB wall installation

Contours at 5, 20, 50,100, 200, 500, and 1000 ug/l



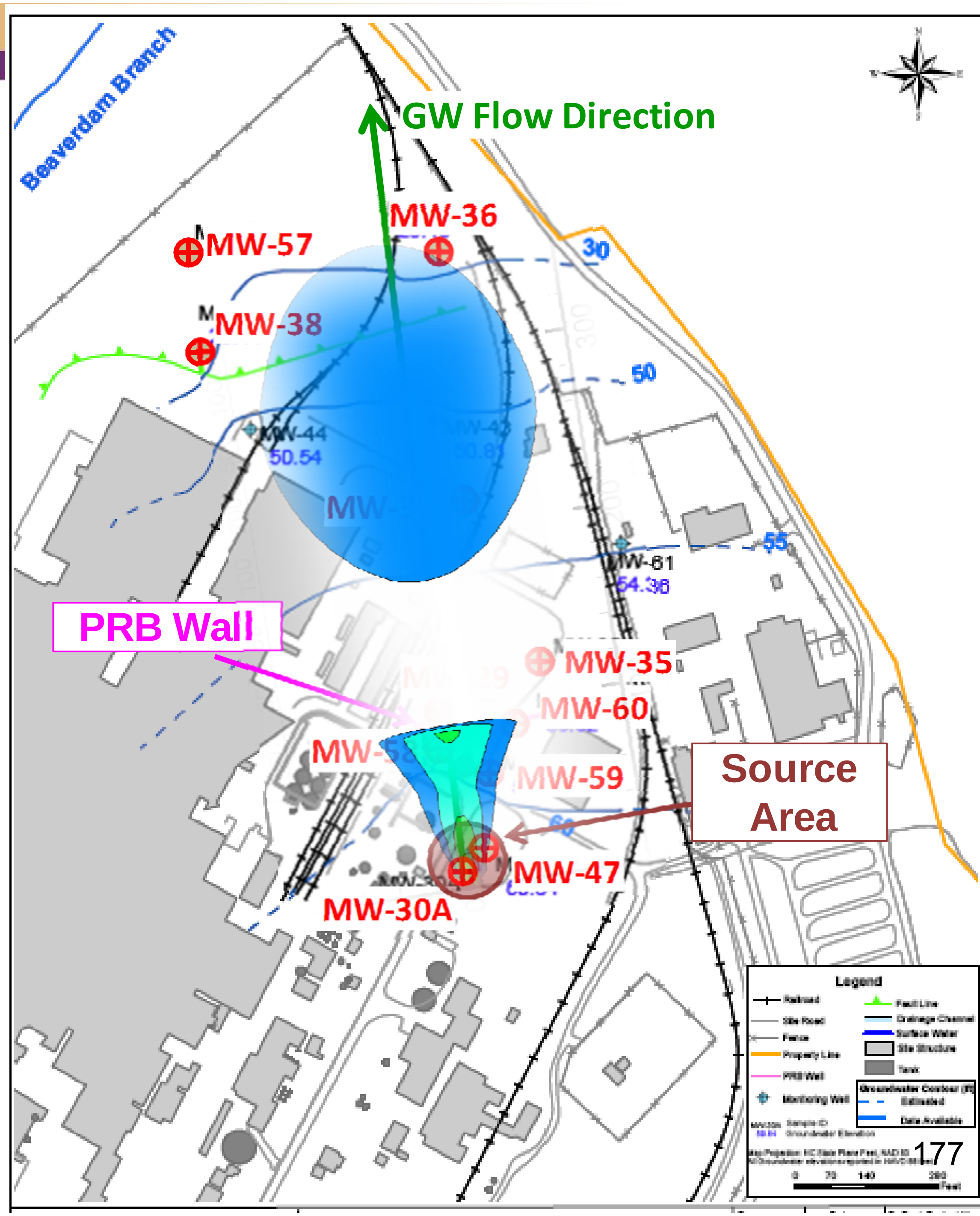
Simulated TCE concentrations In 2001, 2 years after source remediation and PRB wall installation

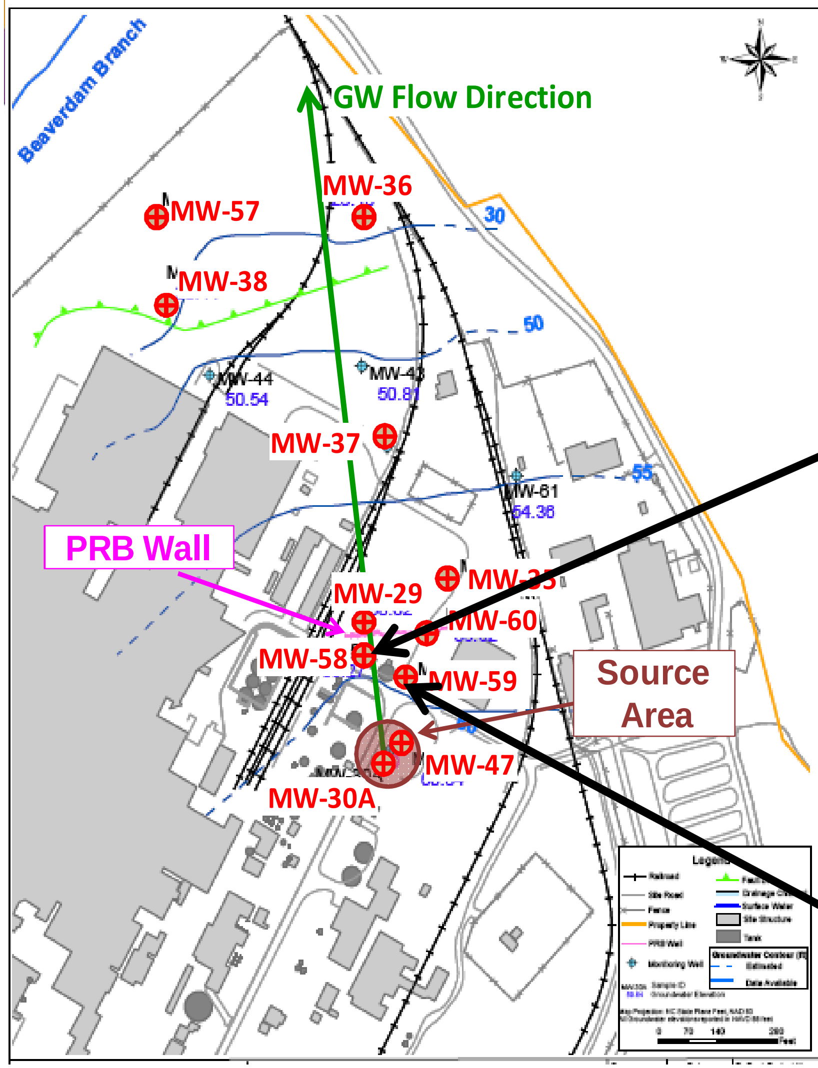
Contours at 5, 20, 50,100, 200, 500, and 1000 ug/l



Simulated TCE concentrations In 2009, 10 years after source remediation and PRB wall installation

Contours at 5, 20, 50,100, 200, 500, and 1000 ug/l




Beaverdam Branch
GW Flow Direction
MW-36
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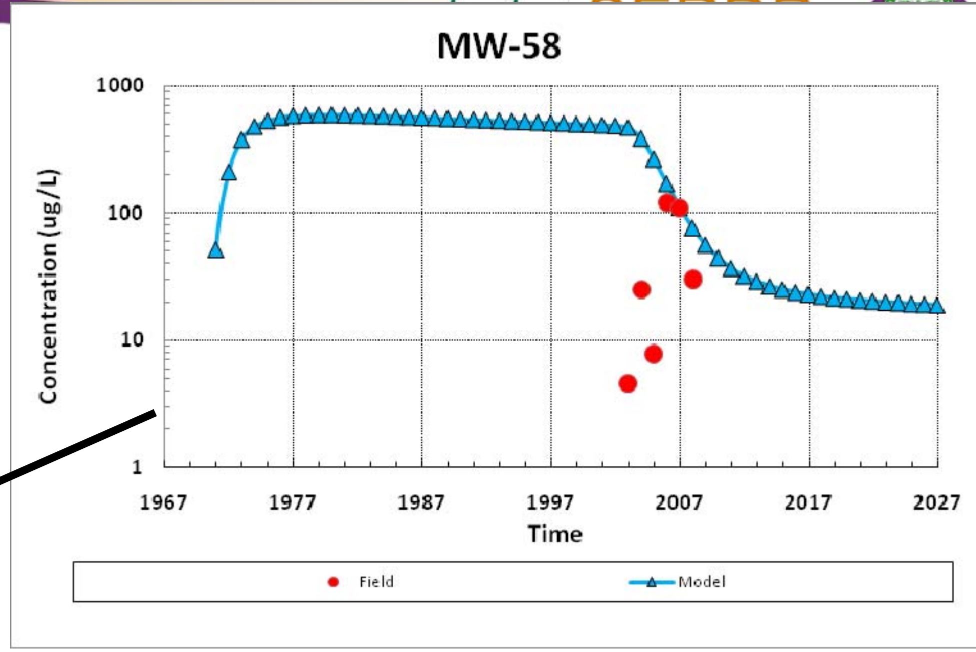
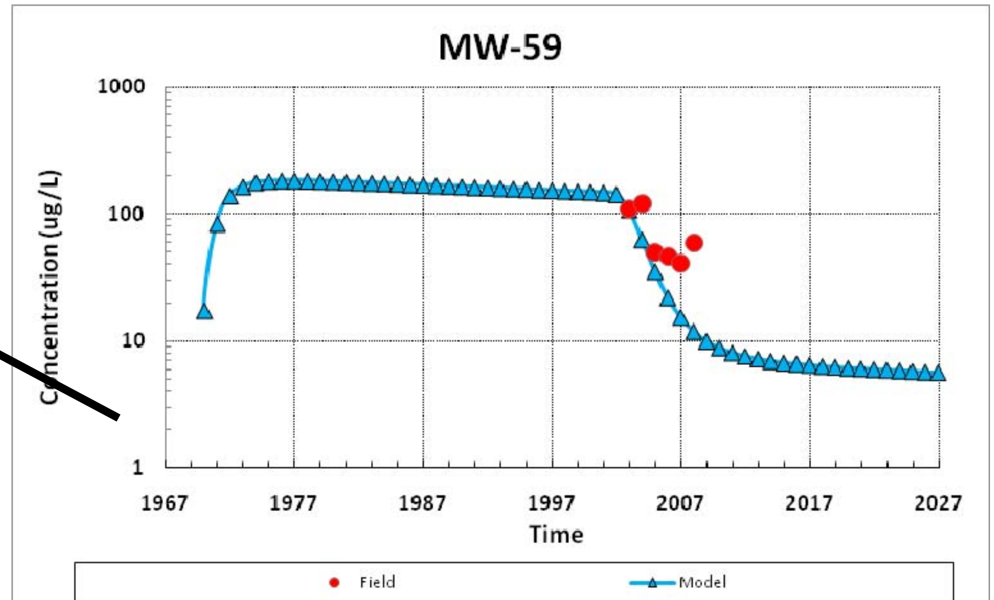
MW-43
50.81
MW-37
55
MW-61
54.38
PRB Wall
MW-29
MW-33
MW-60
MW-58
MW-59
Source
Area
MW-47
MW-30A


MW-58
Concentration (ug/L)
1000
100
10
1
1967
1977
1987
1997
2007
2017
2027
Time
Field
Model


MW-59
Concentration (ug/L)
1000
100
10
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1967
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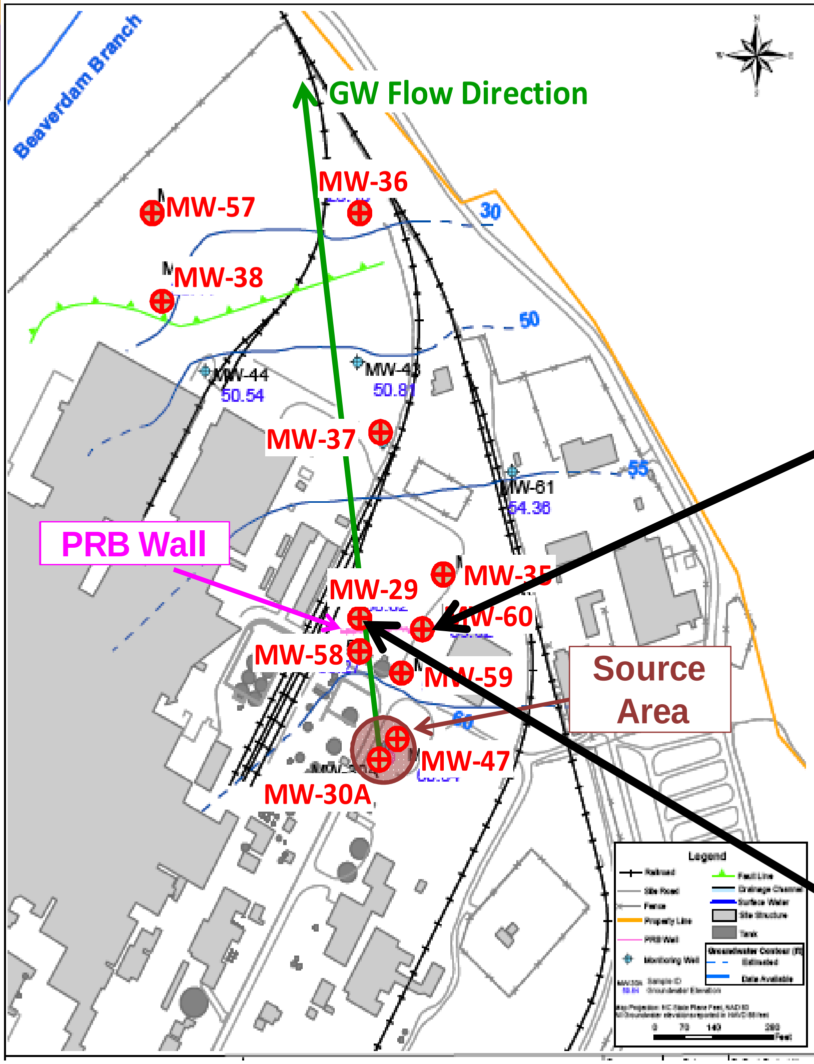
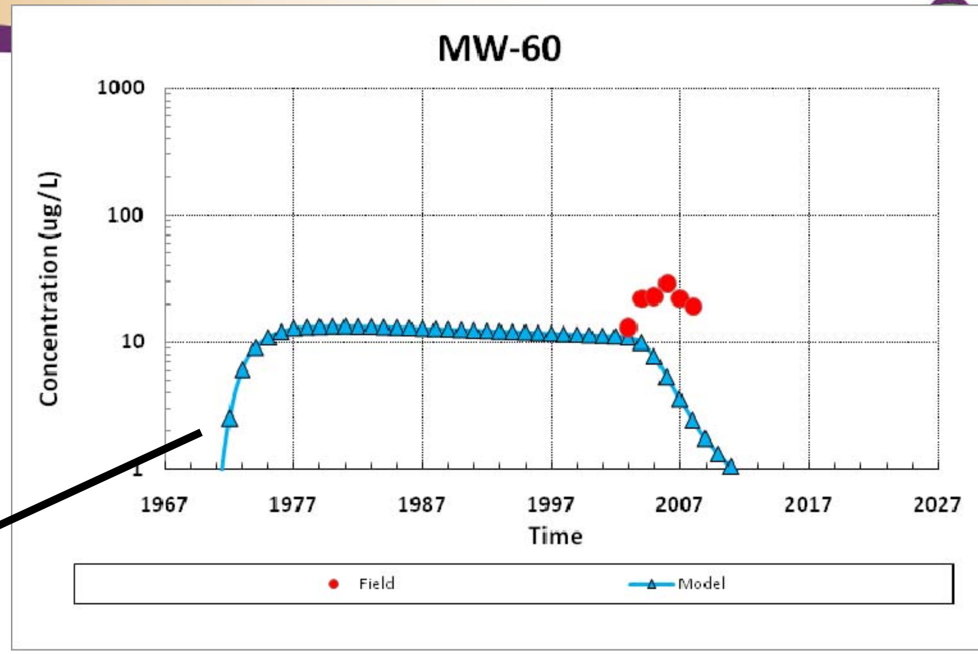
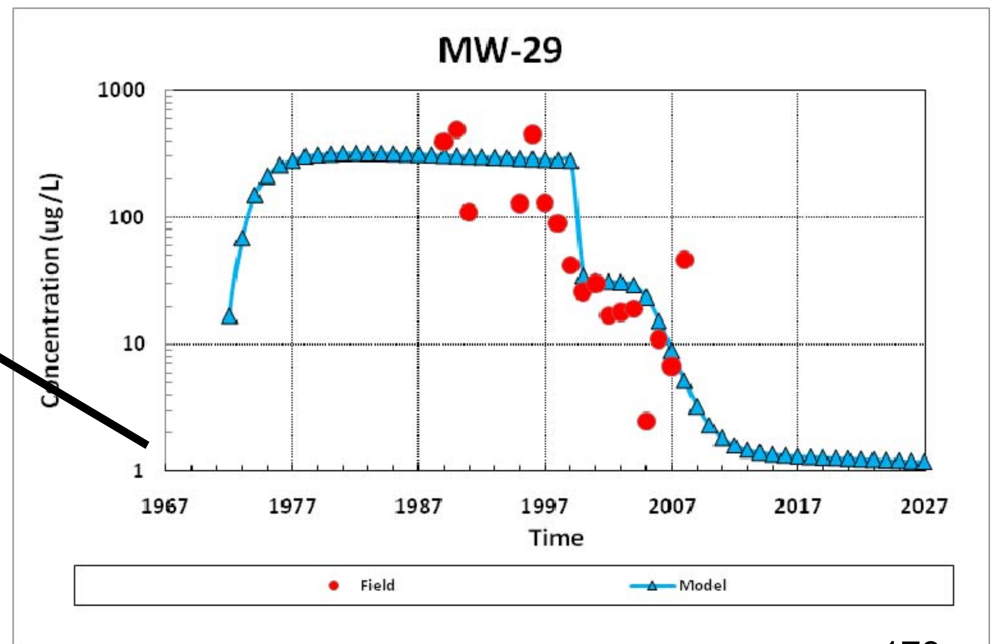
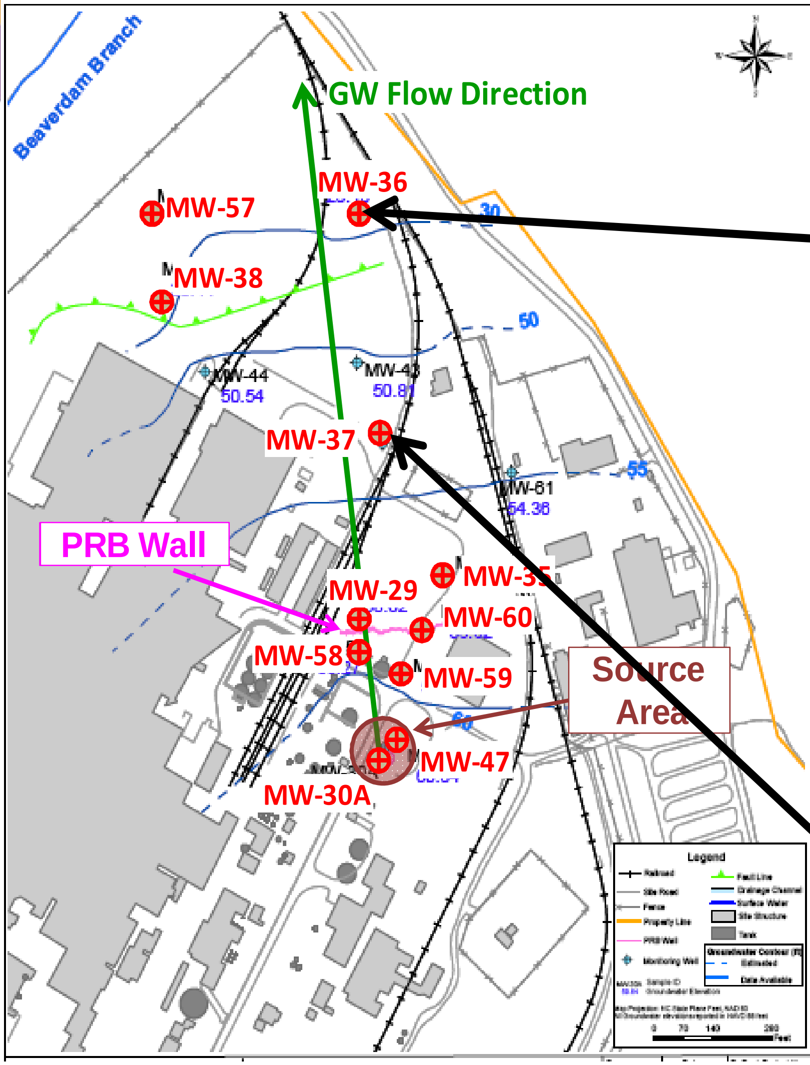
2017
2027
Time
Field
Model

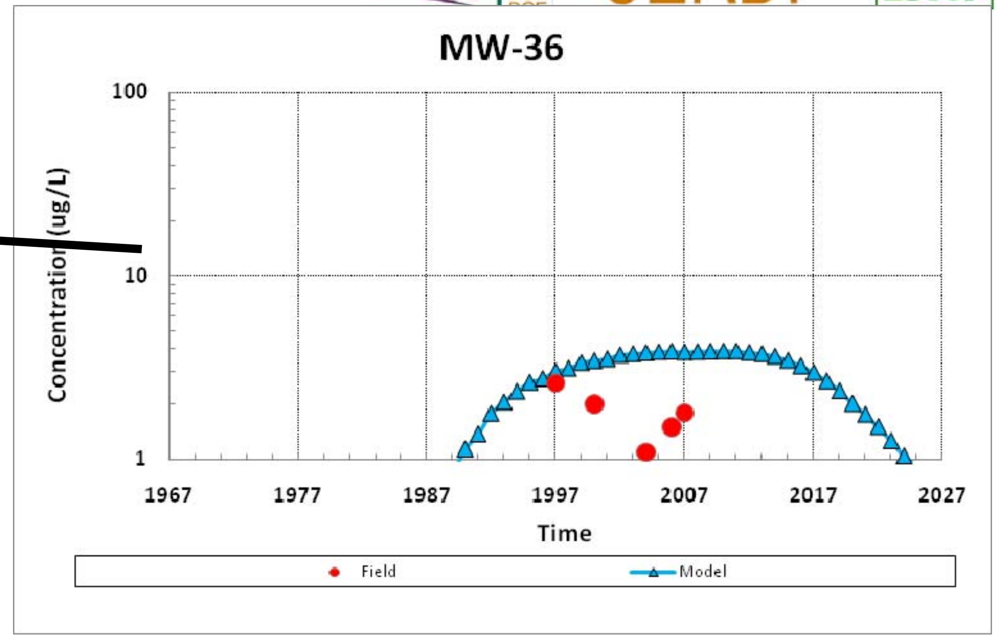


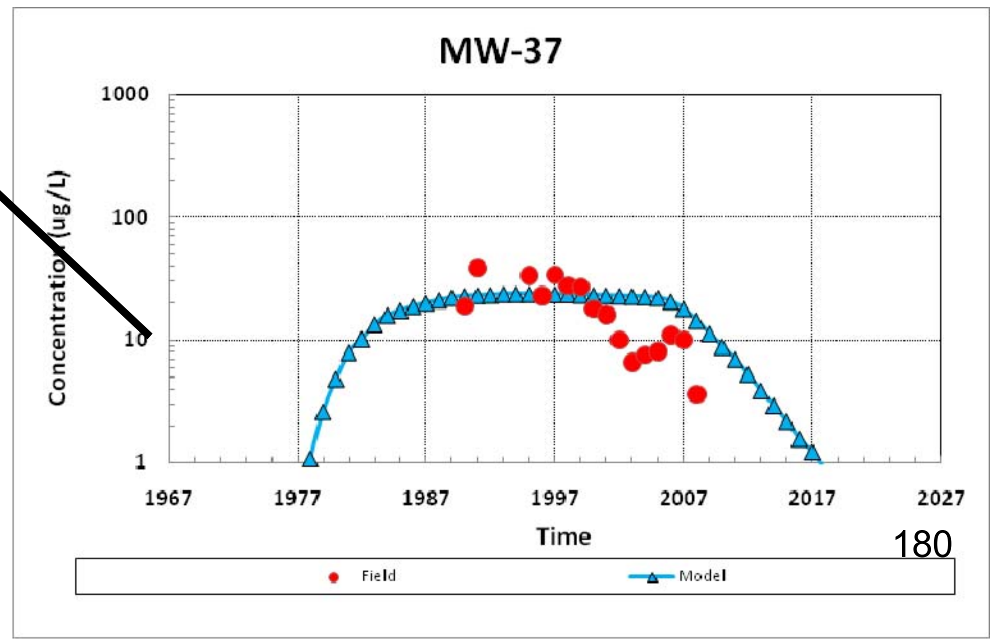




Well MW-29 is just downgradient of PRB wall

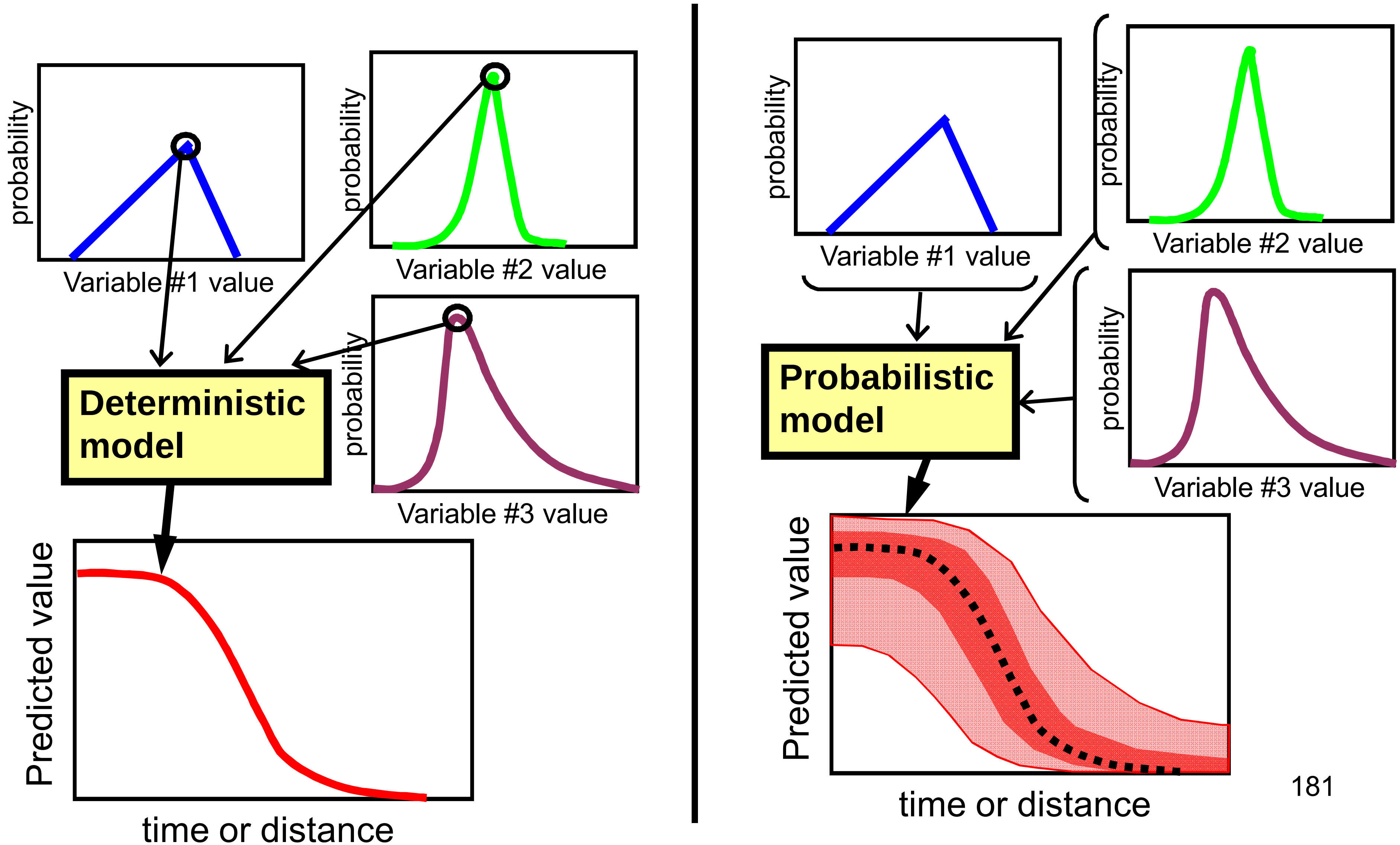




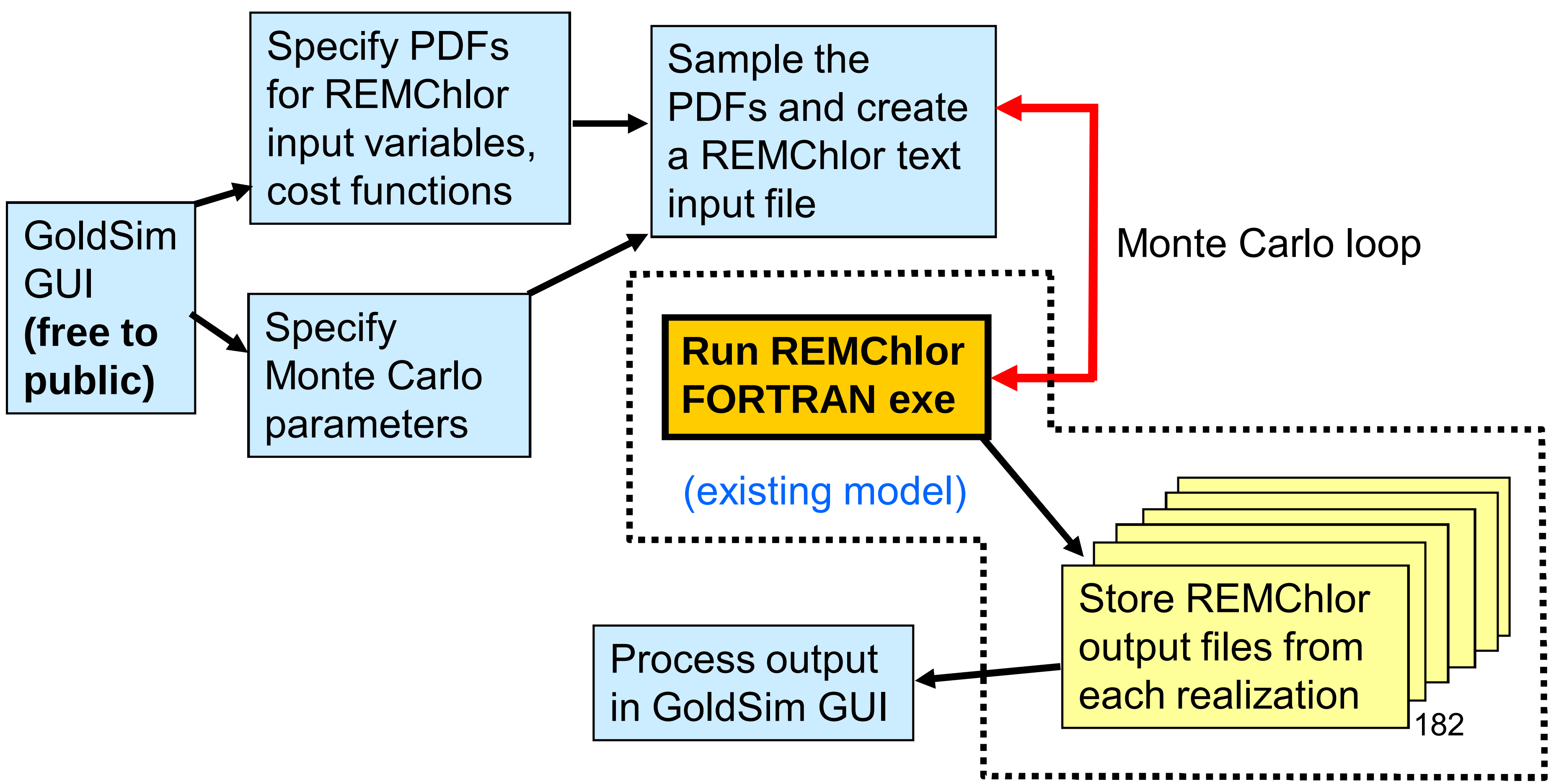


Well MW-29 is just downgradient of PRB wall

Probabilistic Simulation – treat input variables as uncertain parameters using probability density functions (PDFs)



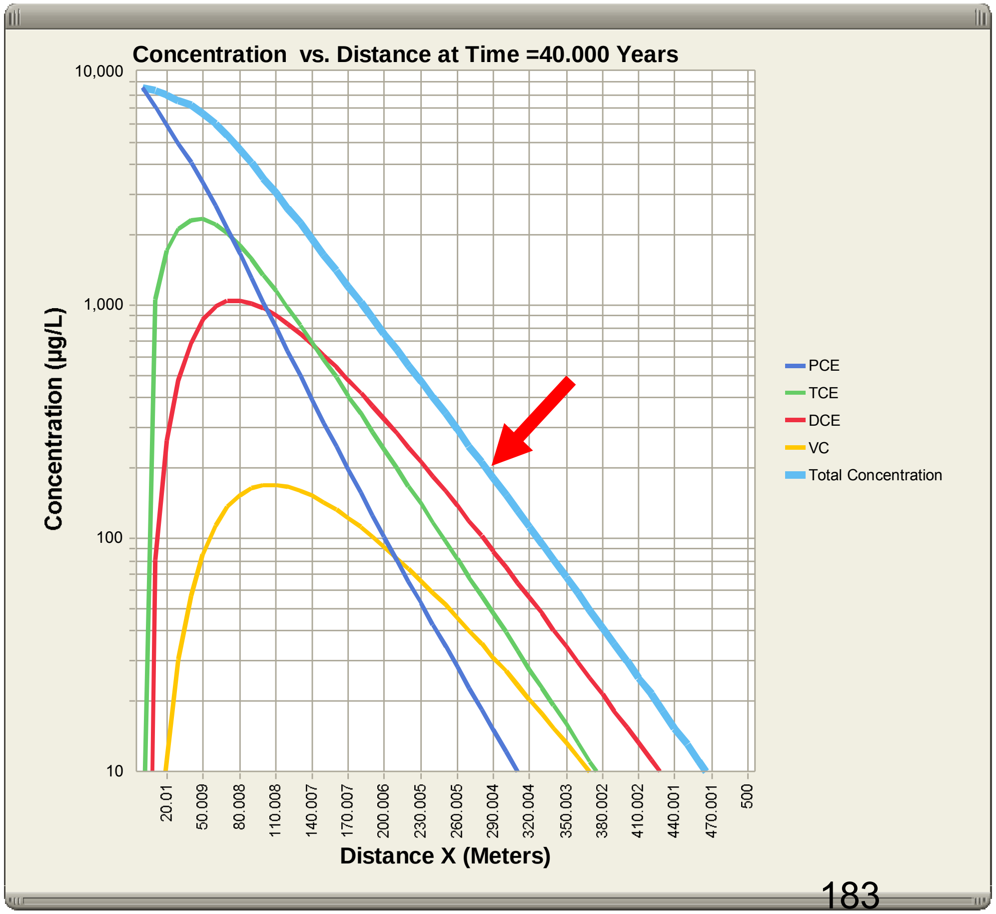
We have coupled the REMChlor FORTRAN code with the GoldSim probabilistic modeling software, and have produced graphical user interface using GoldSim. ***We now have >70 probabilistic variables***



Deterministic REMChlor Example

- 1600 kg release of PCE in 1983
- Plume stabilized in 2001, but is not shrinking
- The 200 ug/l total CVOC contour extends out to 290m in 2008.
- In the next 15 years, the plume will only shrink by 5m without remediation

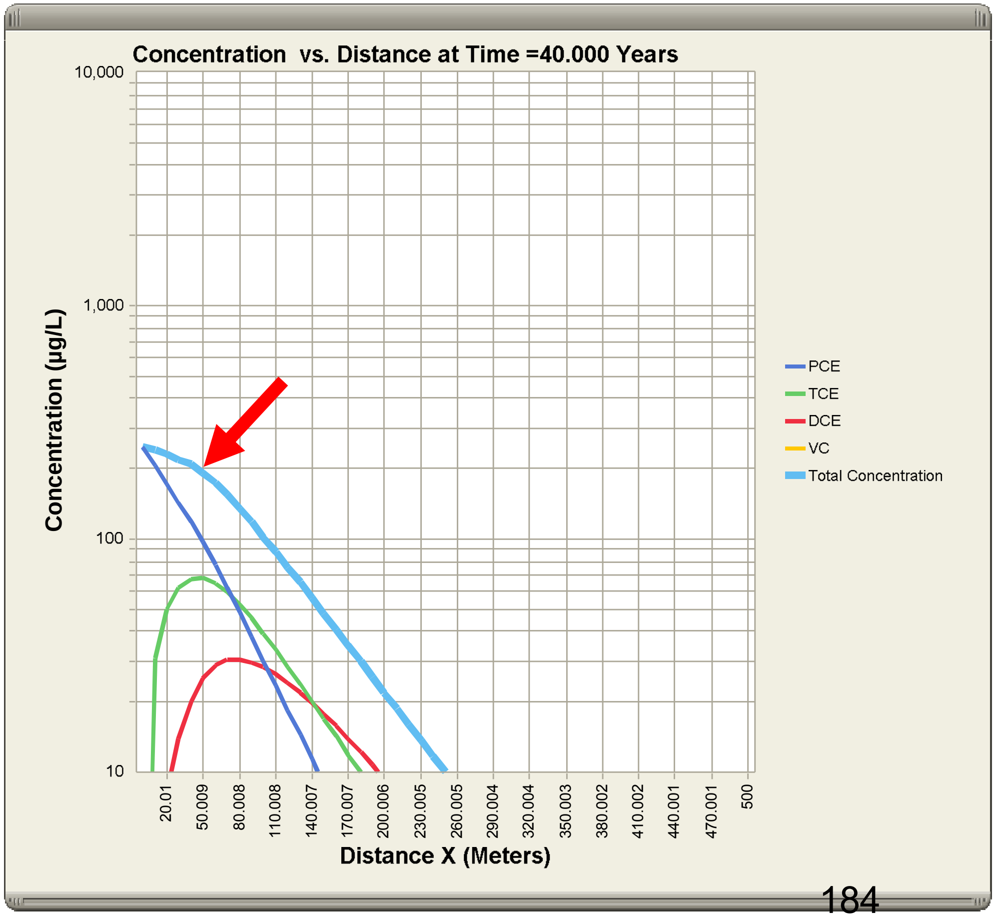
2023



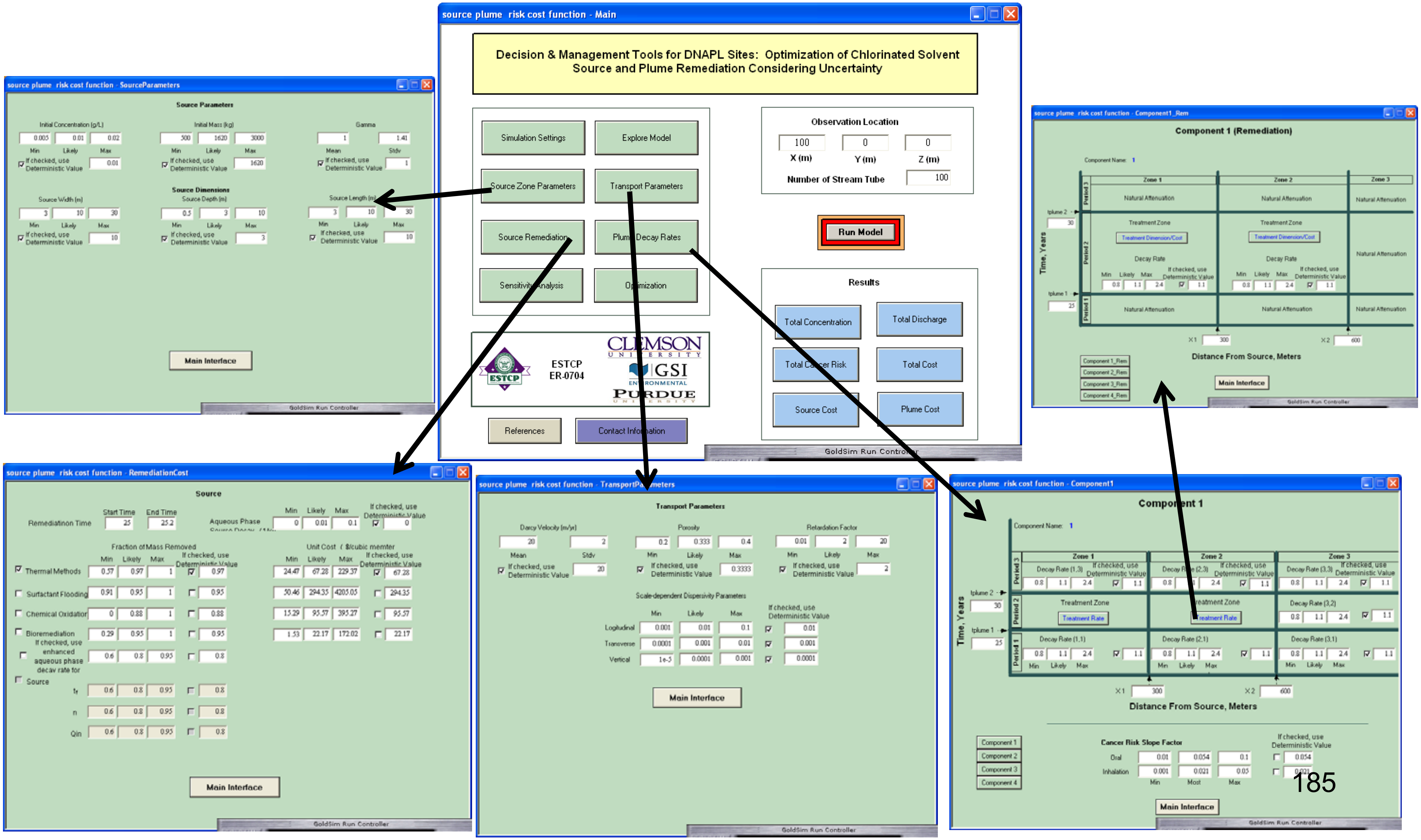
Deterministic REMChlor Example

- Simulate a very effective thermal remediation of the source that removes 97% of the source mass this year
- Remediation goal is to shrink the 200 ug/l contour to less than 100m in 15 years
- Maximum plume extent is only 50m, so this remediation should work

2023

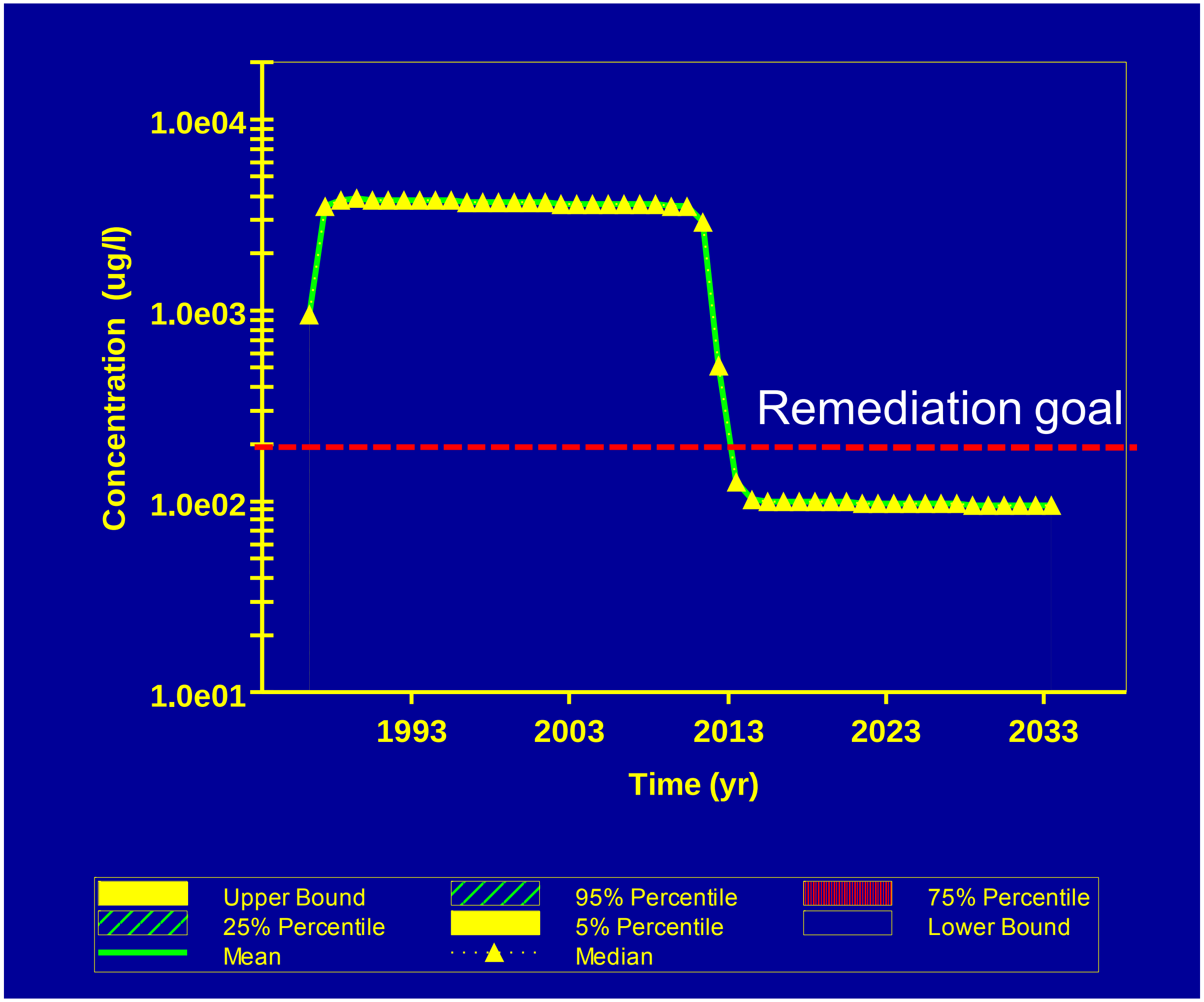


Setup REMChlor-GoldSim to run same problem

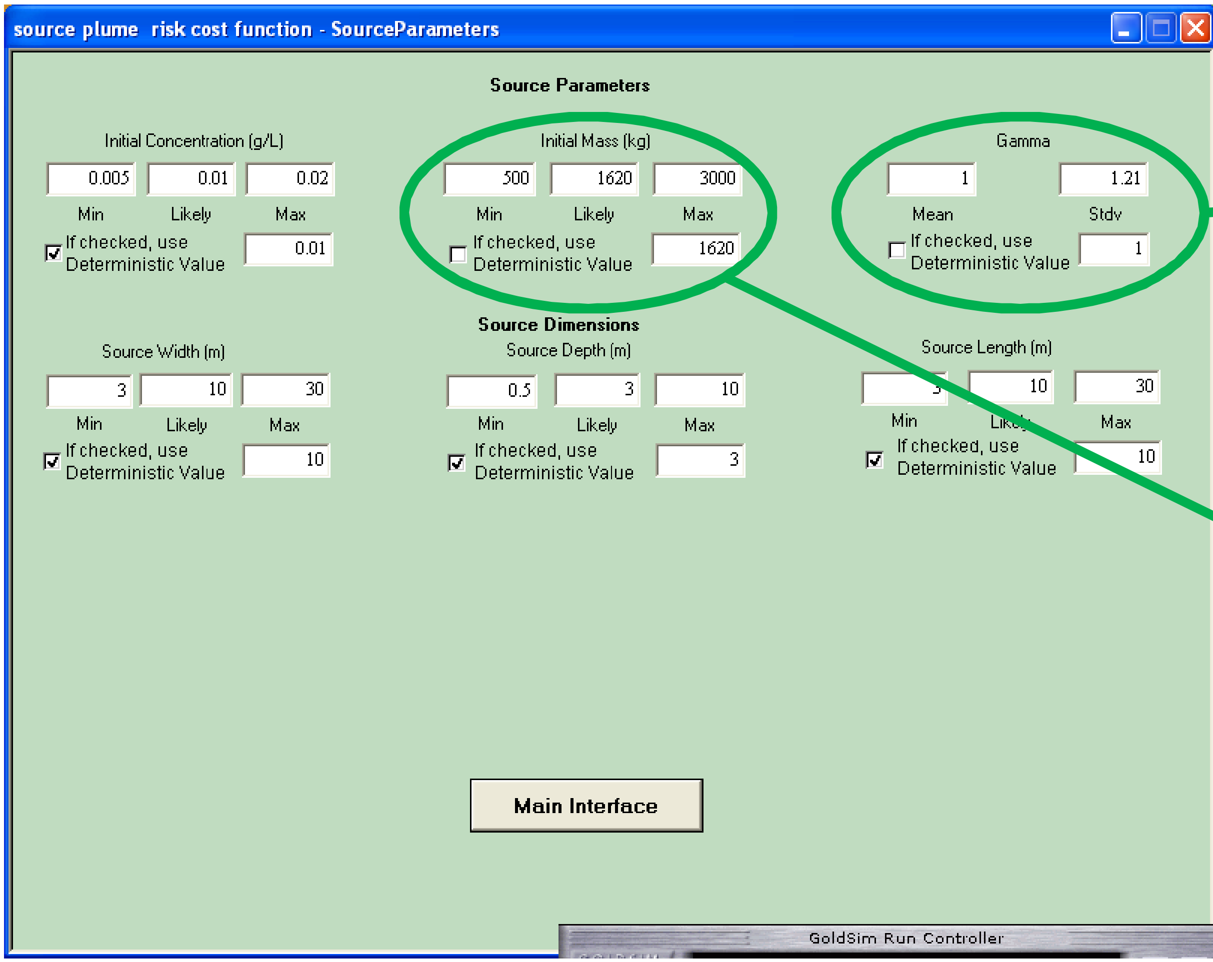


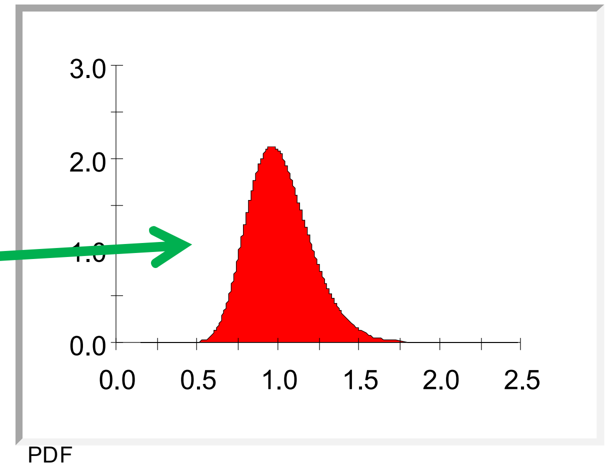
Setup REMChlor-GoldSim to run same problem – deterministic result is the same

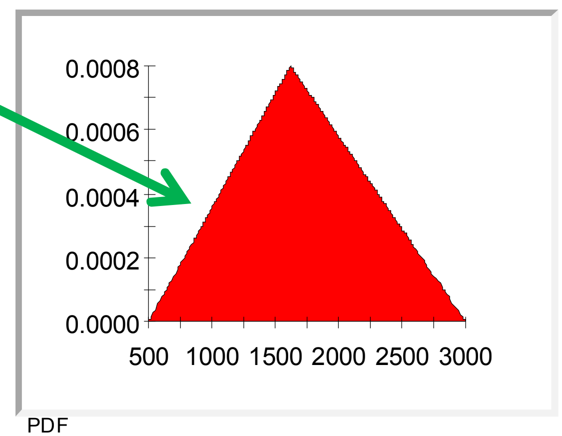
Concentration versus time at compliance point located 100m downgradient from source.



Setup REMChlor-GoldSim to run same problem – make some source parameters uncertain

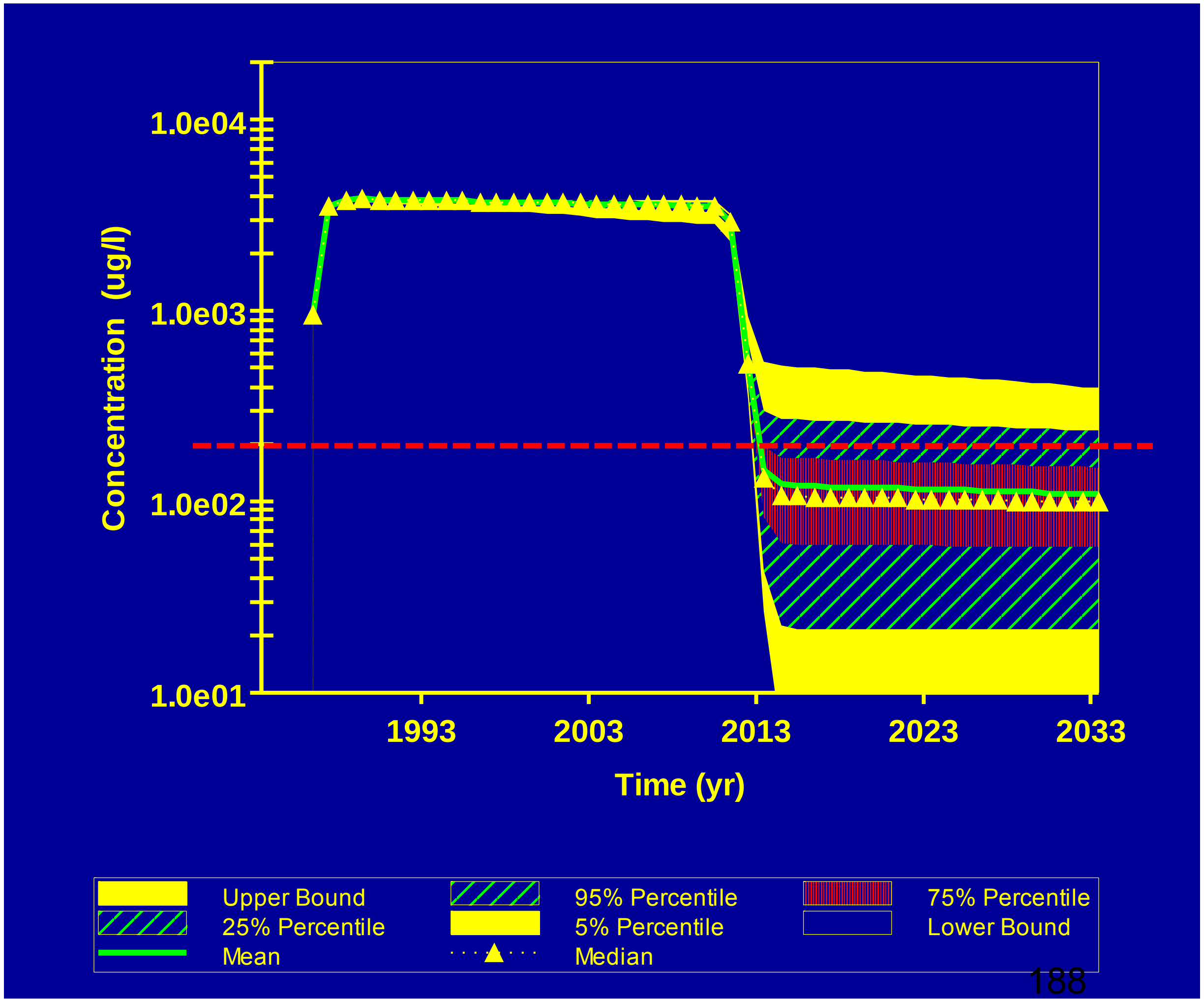




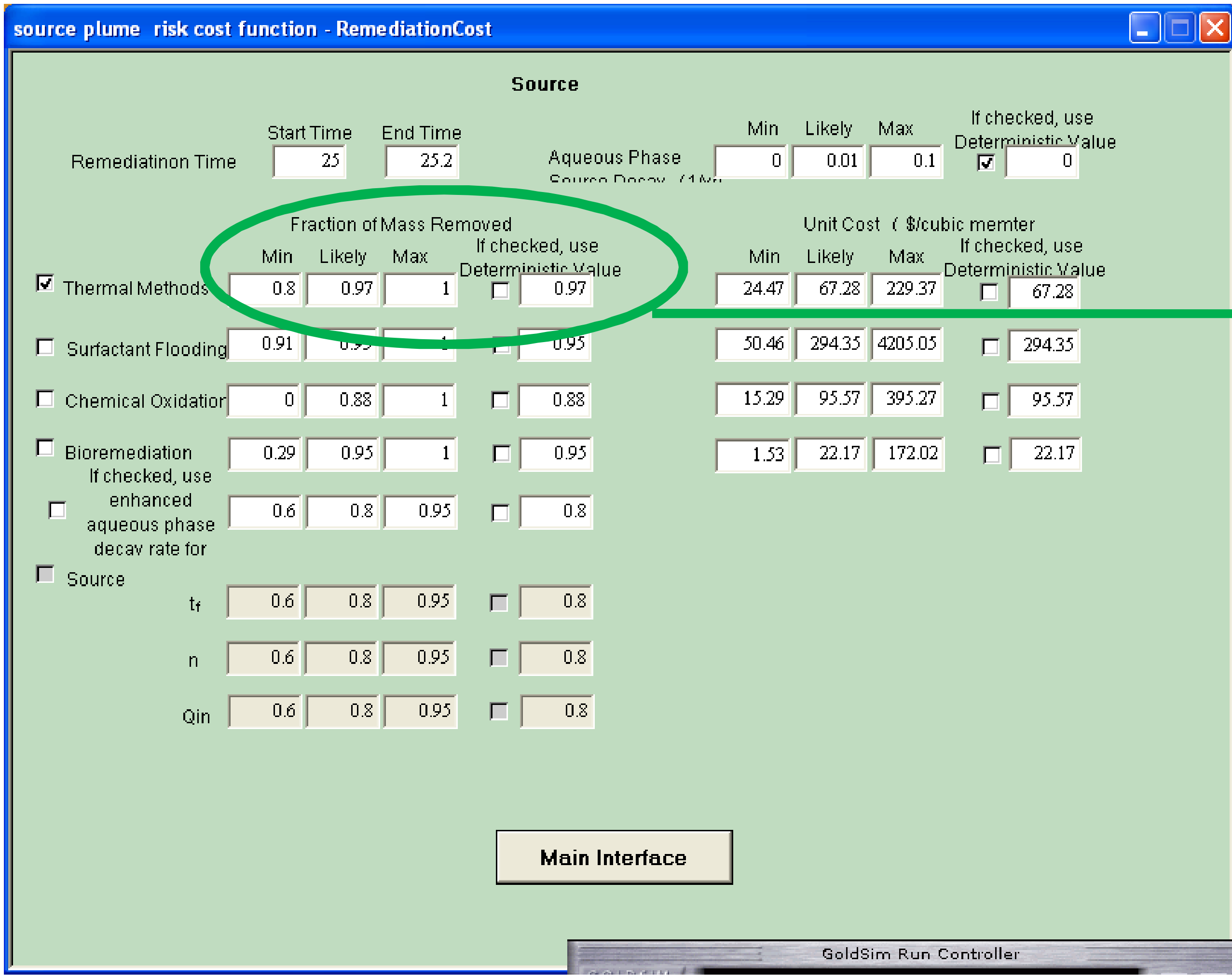


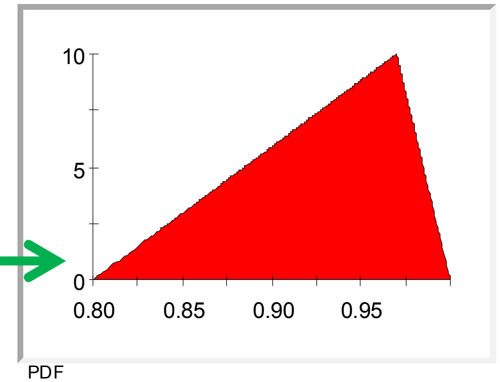
Probabilistic result

- Model predicts >75% chance of meeting concentration goal
- Upper bound concentration at 100m in 2023 is 460 ug/l.



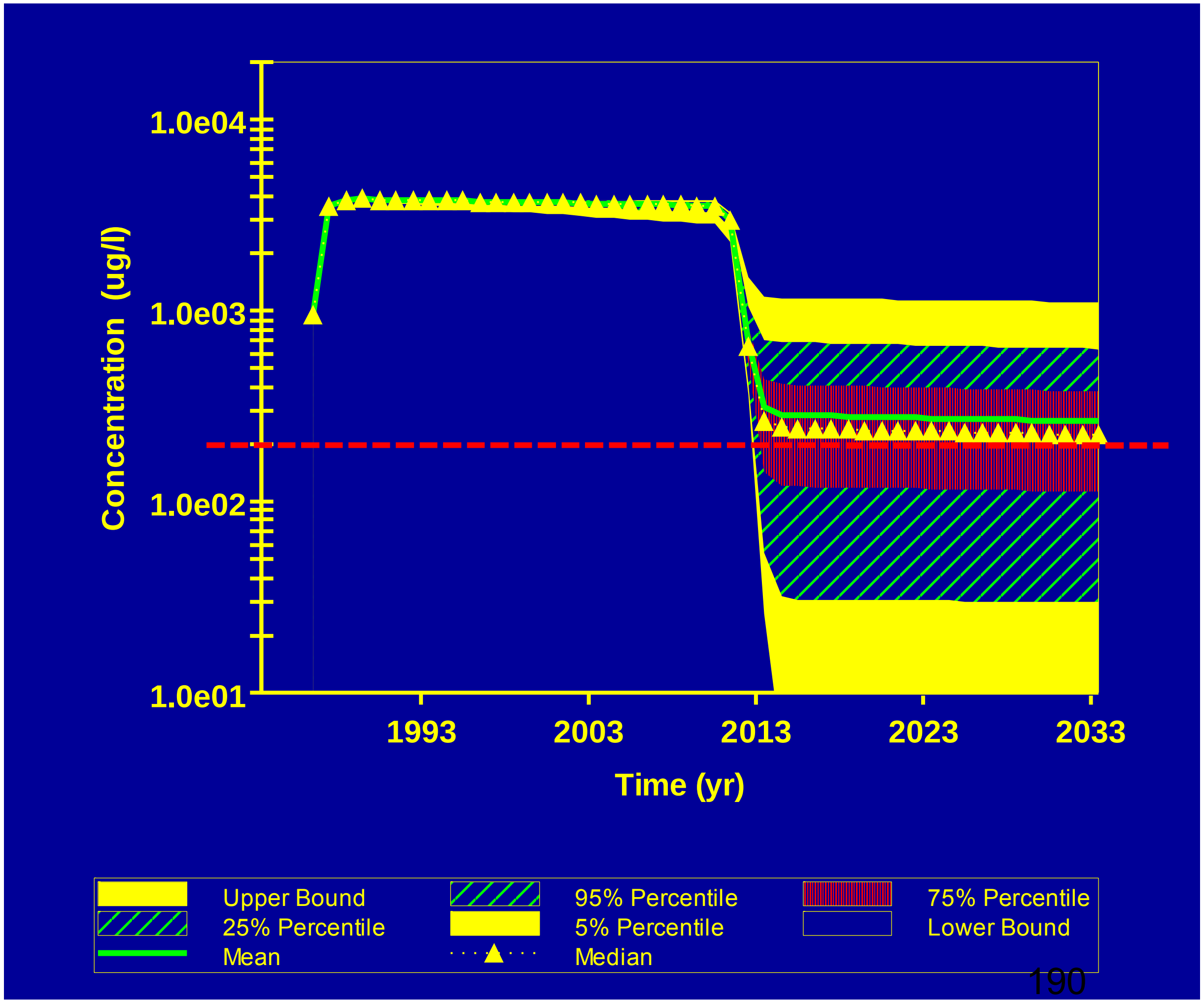
Add remediation efficiency uncertainty



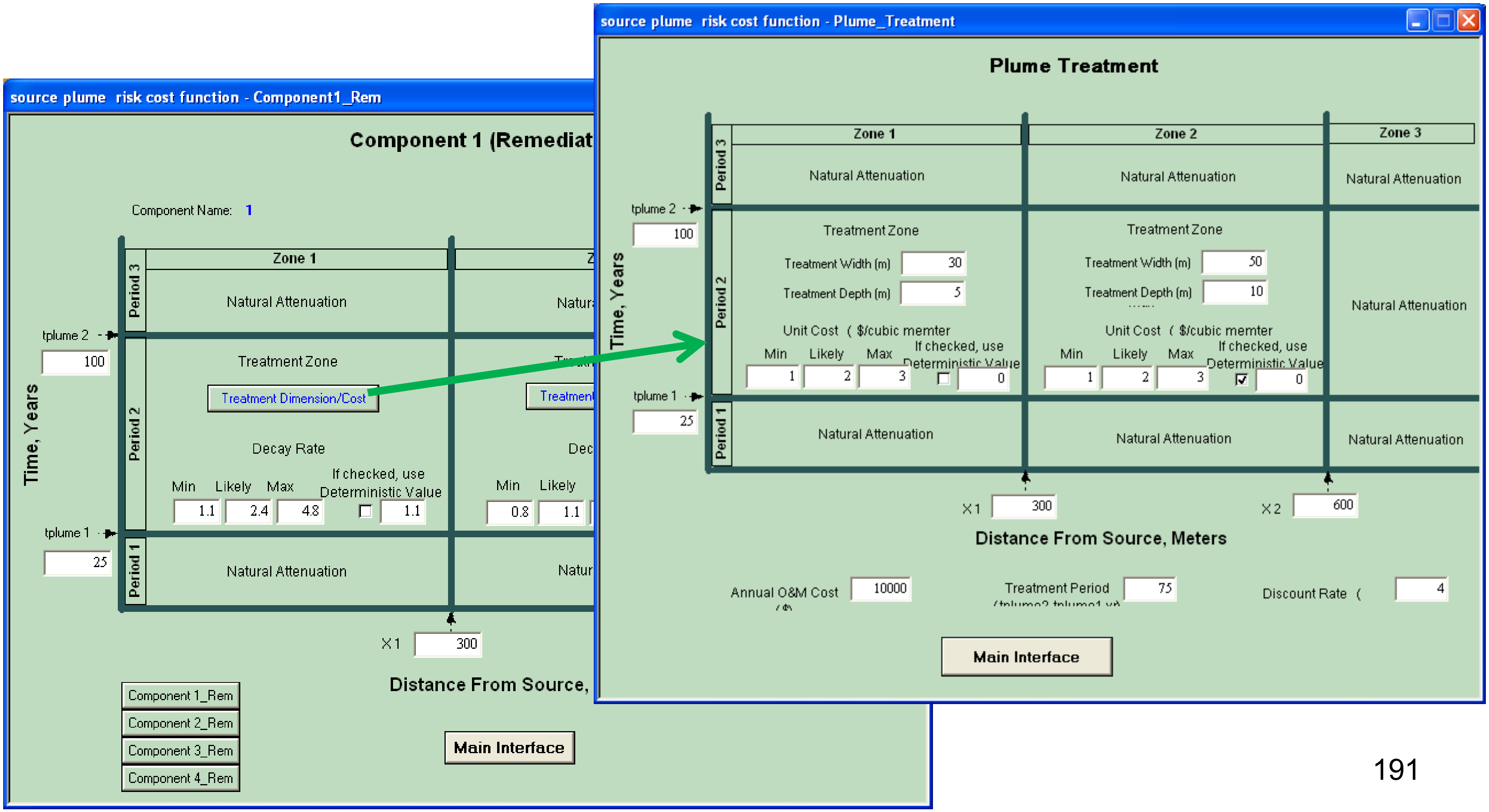


Model predicts possible failure of original design

- Remediation effort is predicted to meet goal only ~50% of the time given uncertainty
- Upper bound concentration at compliance point is 1130 ug/l

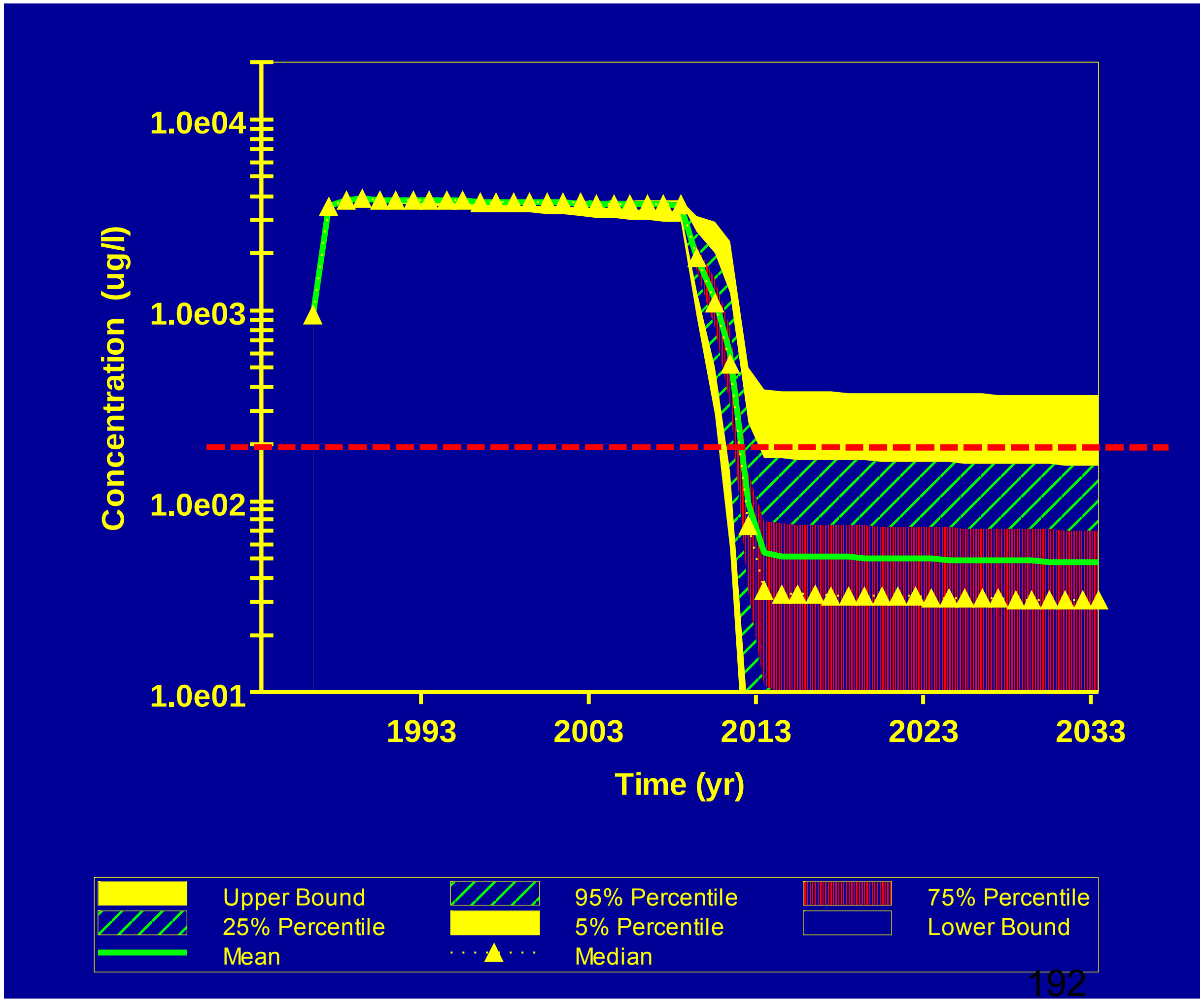


Add enhanced bioremediation of the plume in the first 300m, sustained indefinitely

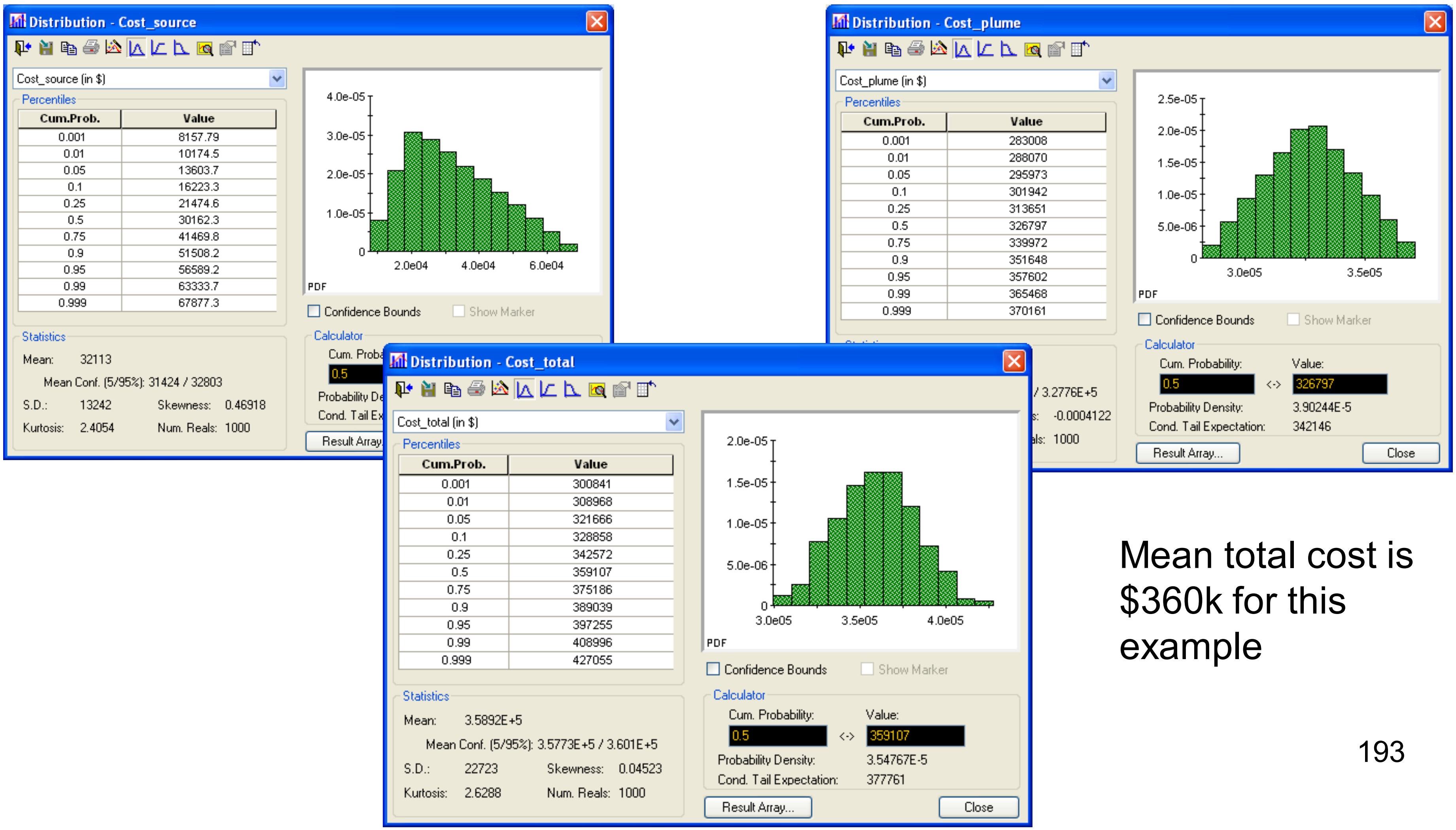


New design appears to be robust

- **Remediation will meet goal with >95% certainty**
- Upper bound concentration at compliance point is 370 ug/l, which is less than a factor of 2 above the goal



Estimated cost of remediaton (using probabilistic cost functions)



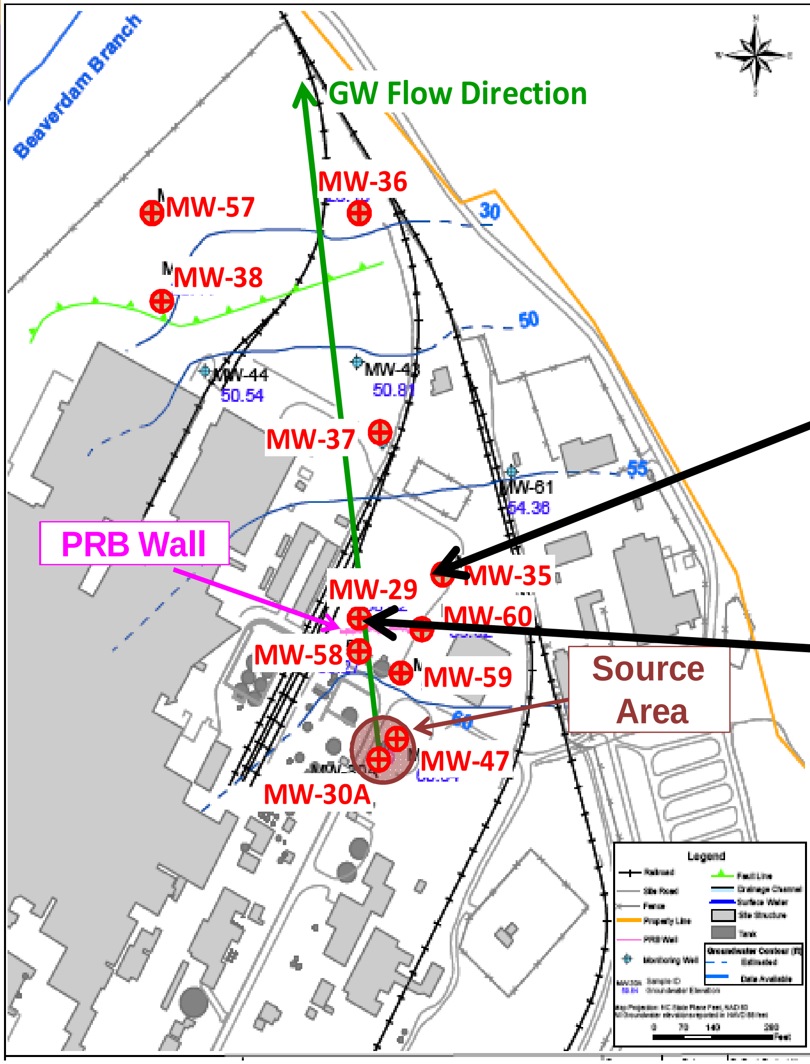
Mean total cost is $360k for this example

Now Revisit the Kinston, NC site

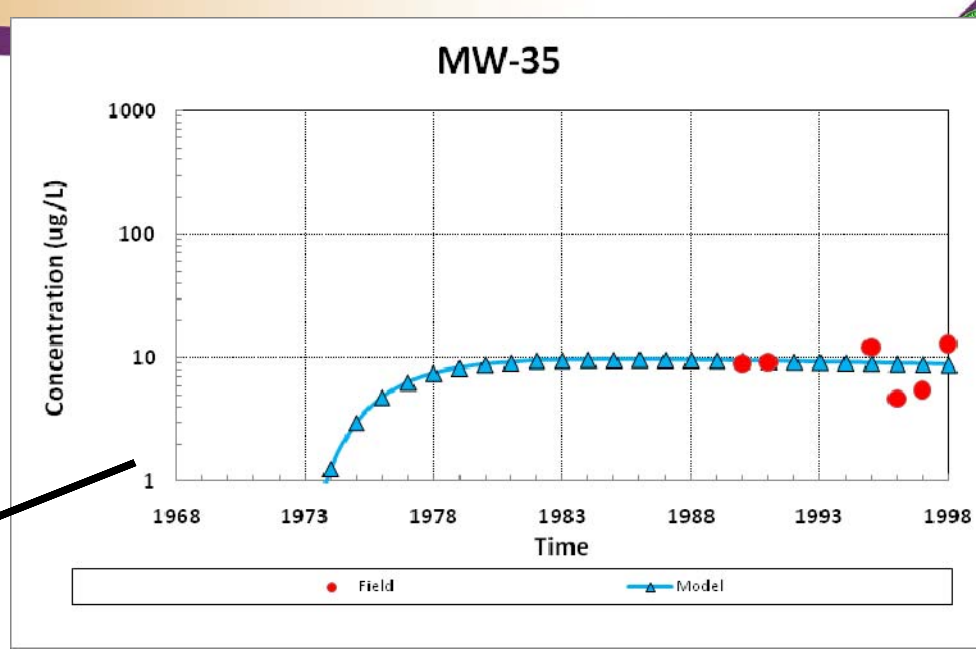
- The earlier example was a calibrated deterministic model
- What if we wanted to predict the response of the system to proposed remediation operations?
- Let's pretend that it is 1998. We have been monitoring this plume for 10 years, so we have some parameter estimates
- We'll use the probabilistic model to simulate the source and plume remediation considering uncertainty

Step 1: Calibrate transport model using pre-1998 data

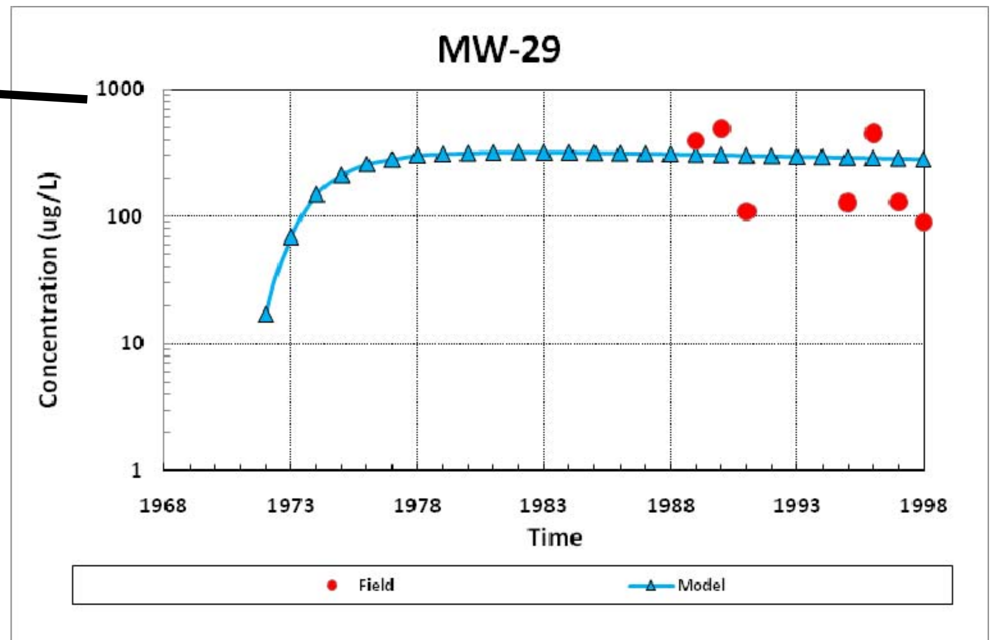
Parameter	Value	Comment
Initial Source Conc., C_o	6,000 ug/l	Estimated from source wells
Initial Source Mass, M_o	136 kg	From site reports; assume 1967 release date
Source function exponent, Γ	1	Estimated
Source Width, W	8m	From site reports
Source Depth, D	3.5m	From site reports
Darcy velocity, V	8m/yr	Calibrated; reports had estimated 1.5 to 4.6 m/yr
Porosity, φ	0.33	From site reports
Retardation Factor, R	2	Estimated
Longitudinal dispersivity, α_l	x/20	Calibrated
Transverse dispersivity, α_t	x/50	Calibrated
Vertical dispersivity, α_v	x/1000	Estimated
TCE decay rate in plume, λ	0.125/yr	Calibrated (equal to $t_{1/2}$ of 5.5 yrs)



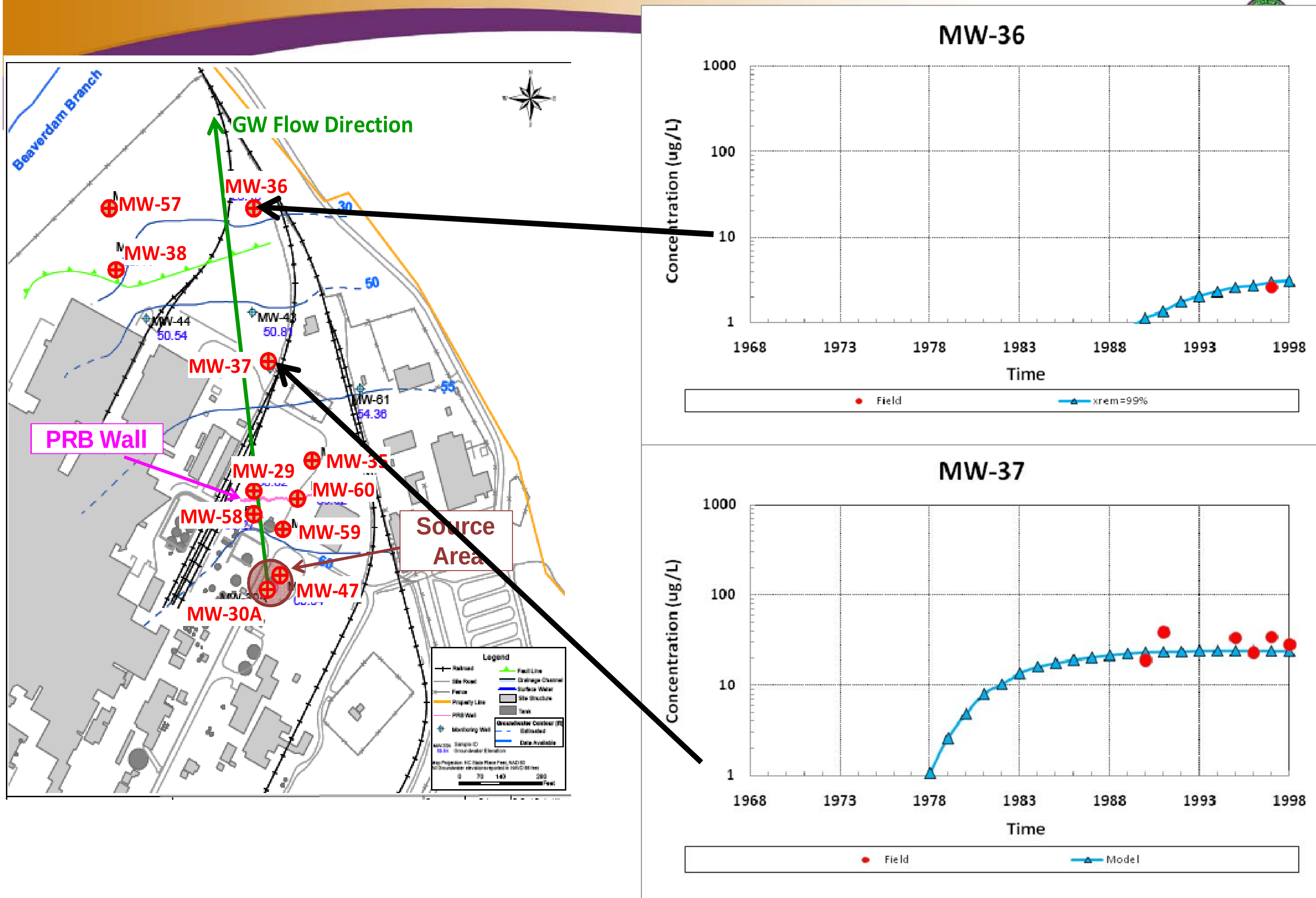
Beaverdam Branch
GW Flow Direction
MW-36
MW-57
MW-38
30
50
MW-44
50.54
MW-43
50.81
MW-37
MW-61
54.38
55
PRB Wall
MW-29
MW-35
MW-60
MW-58
MW-59
Source Area
MW-47
MW-30A
Legend



MW-35
Concentration (ug/L)
1000
100
10
1
1968
1973
1978
1983
1988
1993
1998
Time
Field
Model



MW-29
Concentration (ug/L)
1000
100
10
1
1968
1973
1978
1983
1988
1993
1998
Time
Field
Model

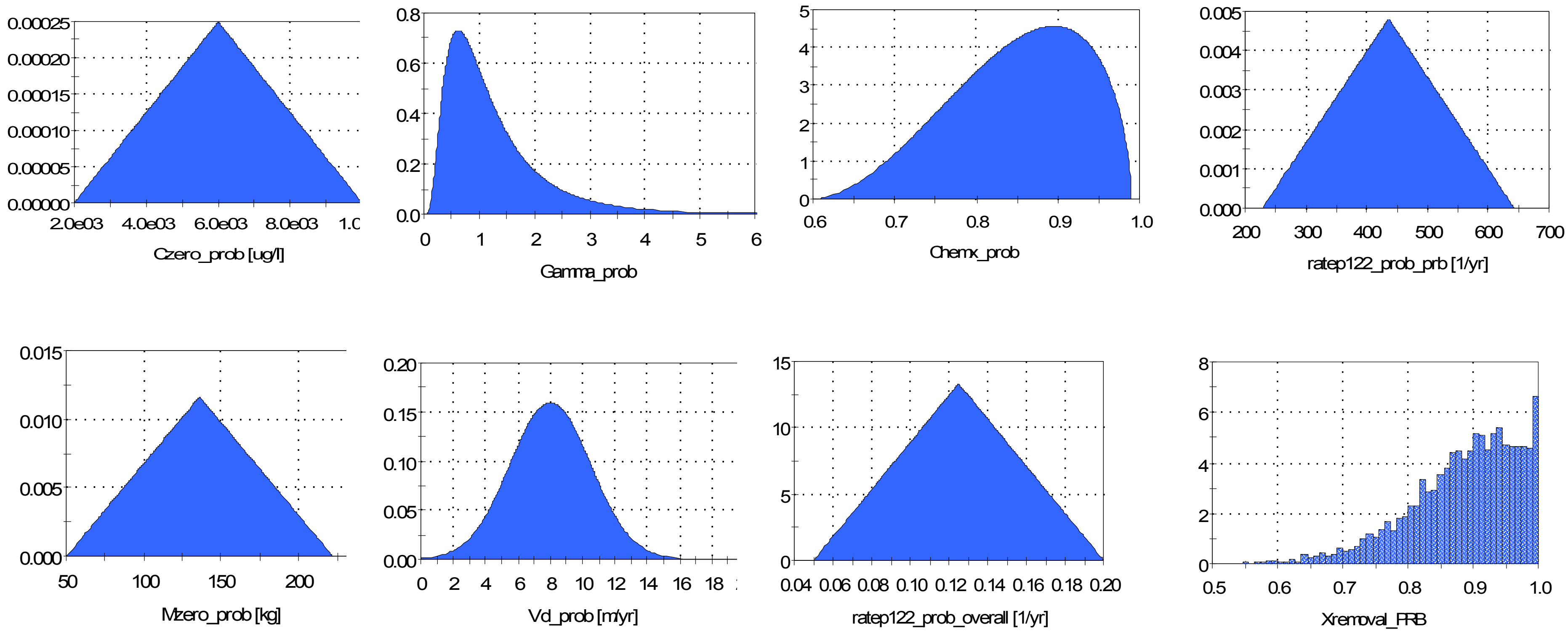


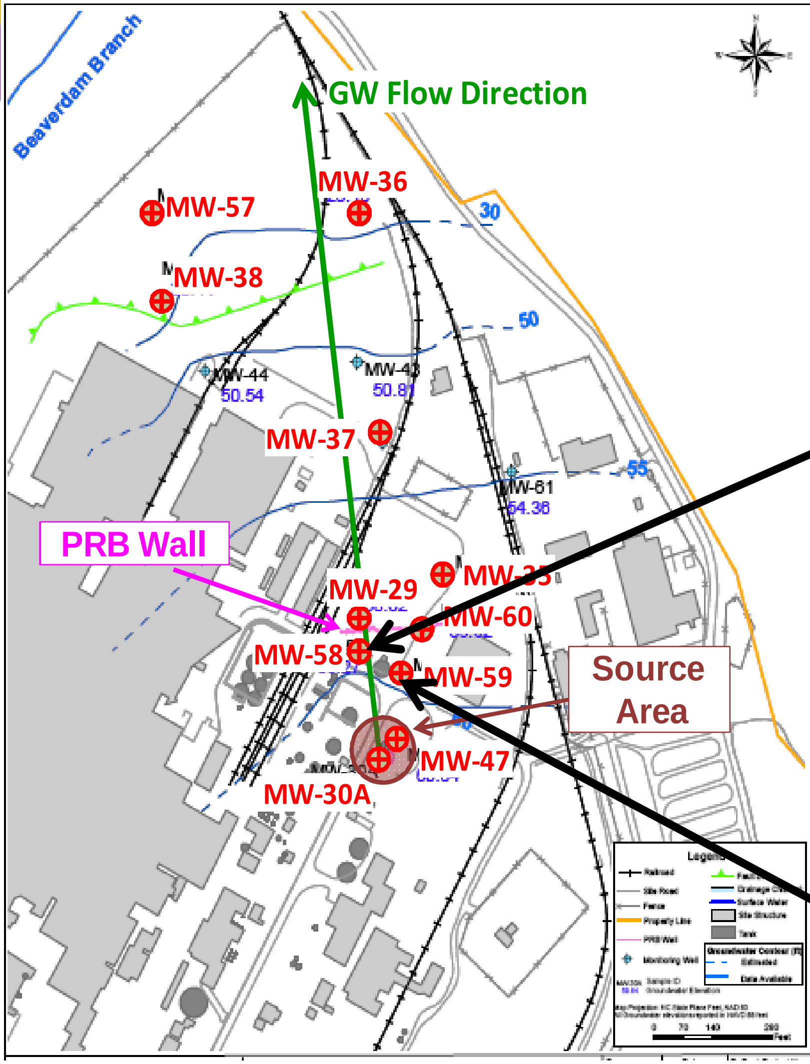
Beaverdam Branch
GW Flow Direction
MW-36
MW-57
MW-38
MW-44
50.54
MW-42
50.81
MW-37
MW-61
54.38
PRB Wall
MW-29
MW-35
MW-60
MW-58
MW-59
Source Area
MW-47
MW-30A
30
50
55
60
Legend
MW-36
1000
100
10
1
Concentration (ug/L)
1968
1973
1978
1983
1988
1993
1998
Time
Field
xrem=99%
MW-37
1000
100
10
1
Concentration (ug/L)
1968
1973
1978
1983
1988
1993
1998
Time
Field
Model

Add Probabilistic Inputs

Parameters	Distribution	Distribution Parameters	Reference
Initial source concentration (ug/l)	Triangular	most likely=6000, min=2000, max=10,000	estimated
Initial source mass (kg)	Triangular	most likely=136, min=50, max=222	estimated
Power function exponent	Log-normal	geo. Mean =1, geo stdv=2	
Darcy velocity (m/yr)	Normal	mean=8, stdv=2.5	
Overall plume natural attenuation rate for TCE (1/yr)	Triangular	most likely=0.125, min=0.05, max=0.2	
Fraction of source mass removal (%)	Beta	mean=0.85, stdv = 0.08, min=0.6, max=0.99	McGuire et al, 2006
PRB enhanced decay rate (1/yr)	Triangular	most likely=436, min=228, max=643	

PDFs


Czero_prob [ug/l]
Gamma_prob
Chemx_prob
ratep122_prob_prb [1/yr]
Mzero_prob [kg]
Vd_prob [m/yr]
ratep122_prob_overall [1/yr]
Xremoval_FRB


Beaverdam Branch
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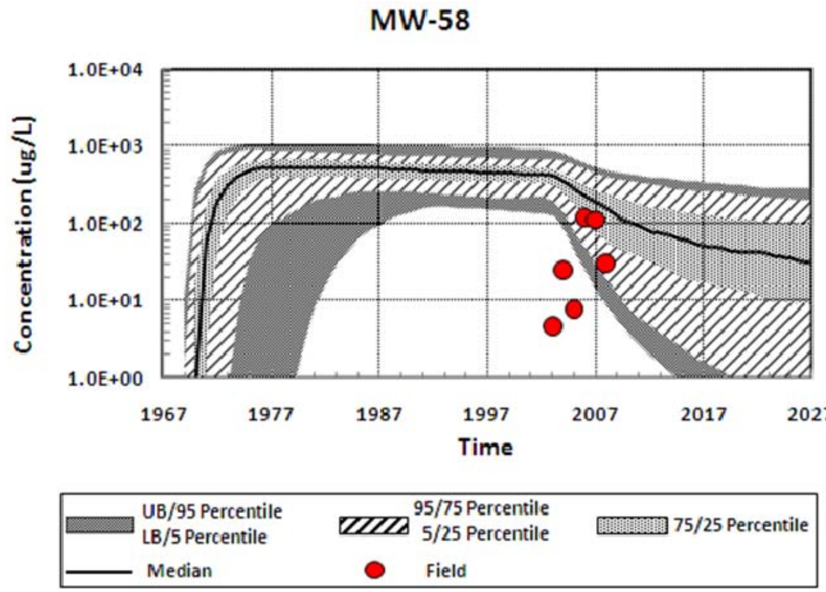
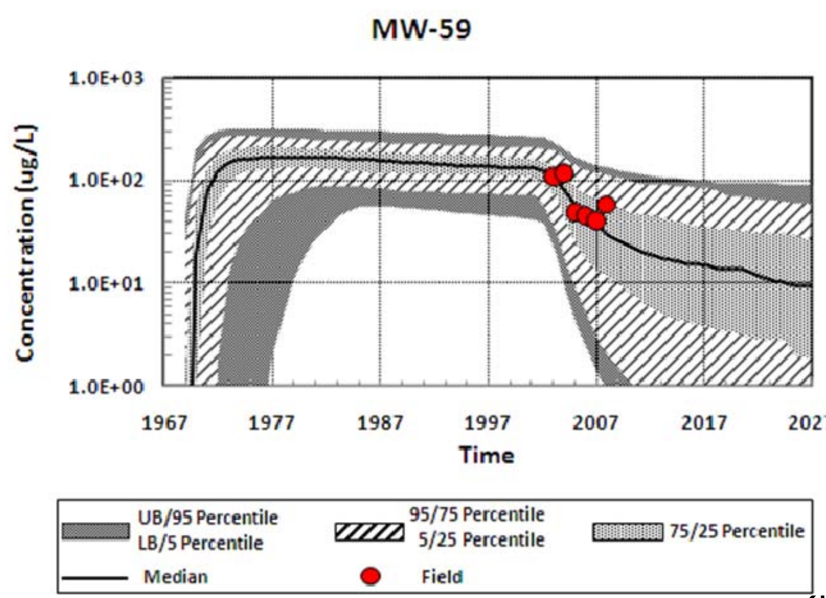
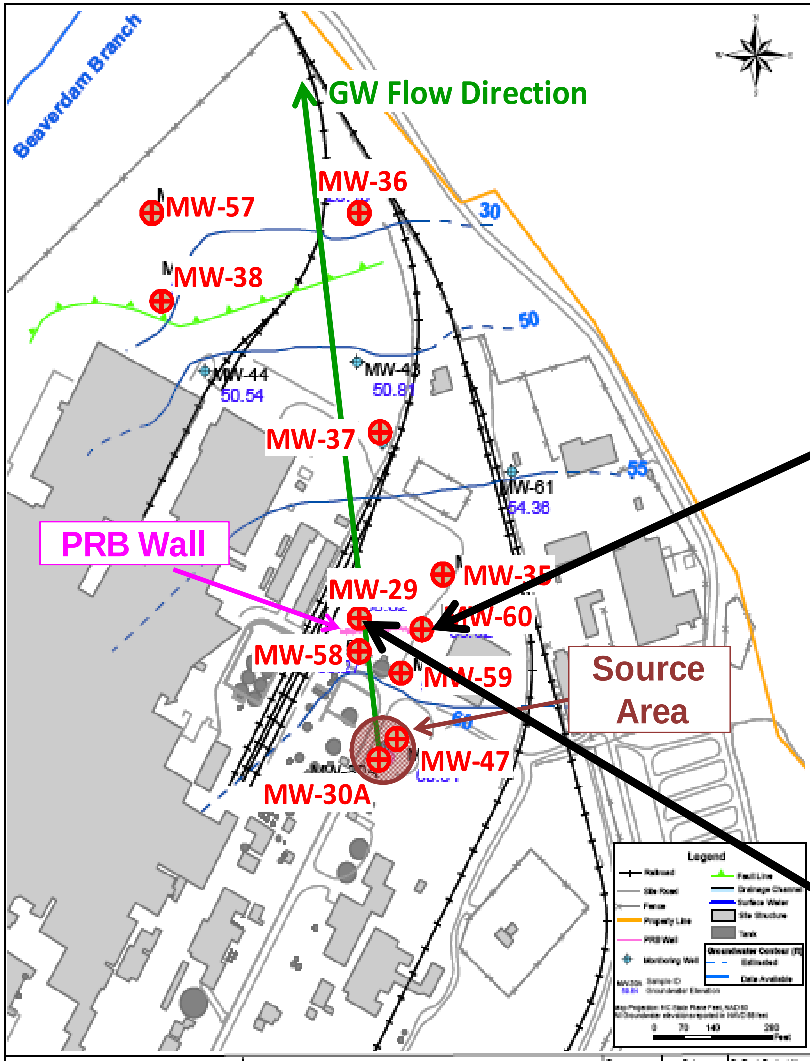
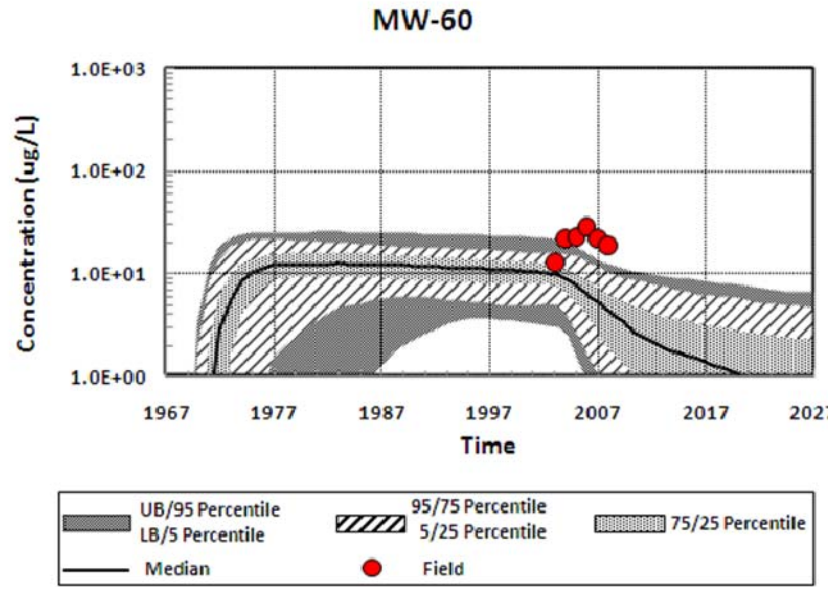
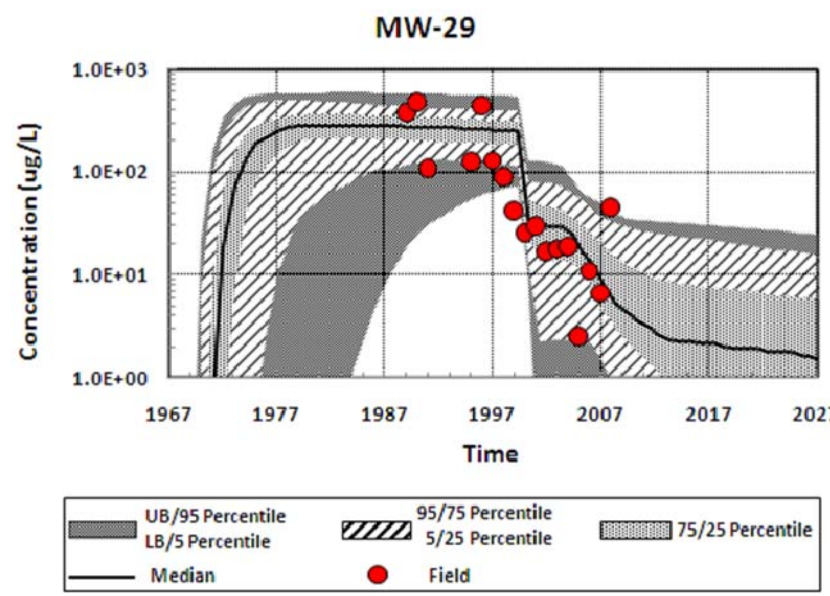
MW-60
MW-58
MW-59
Source Area
MW-47
MW-30A
Legend


MW-58
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Concentration (ug/L)
1967
1977
1987
1997
2007
2017
2027
Time
UB/95 Percentile
LB/5 Percentile
95/75 Percentile
5/25 Percentile
75/25 Percentile
Median
Field

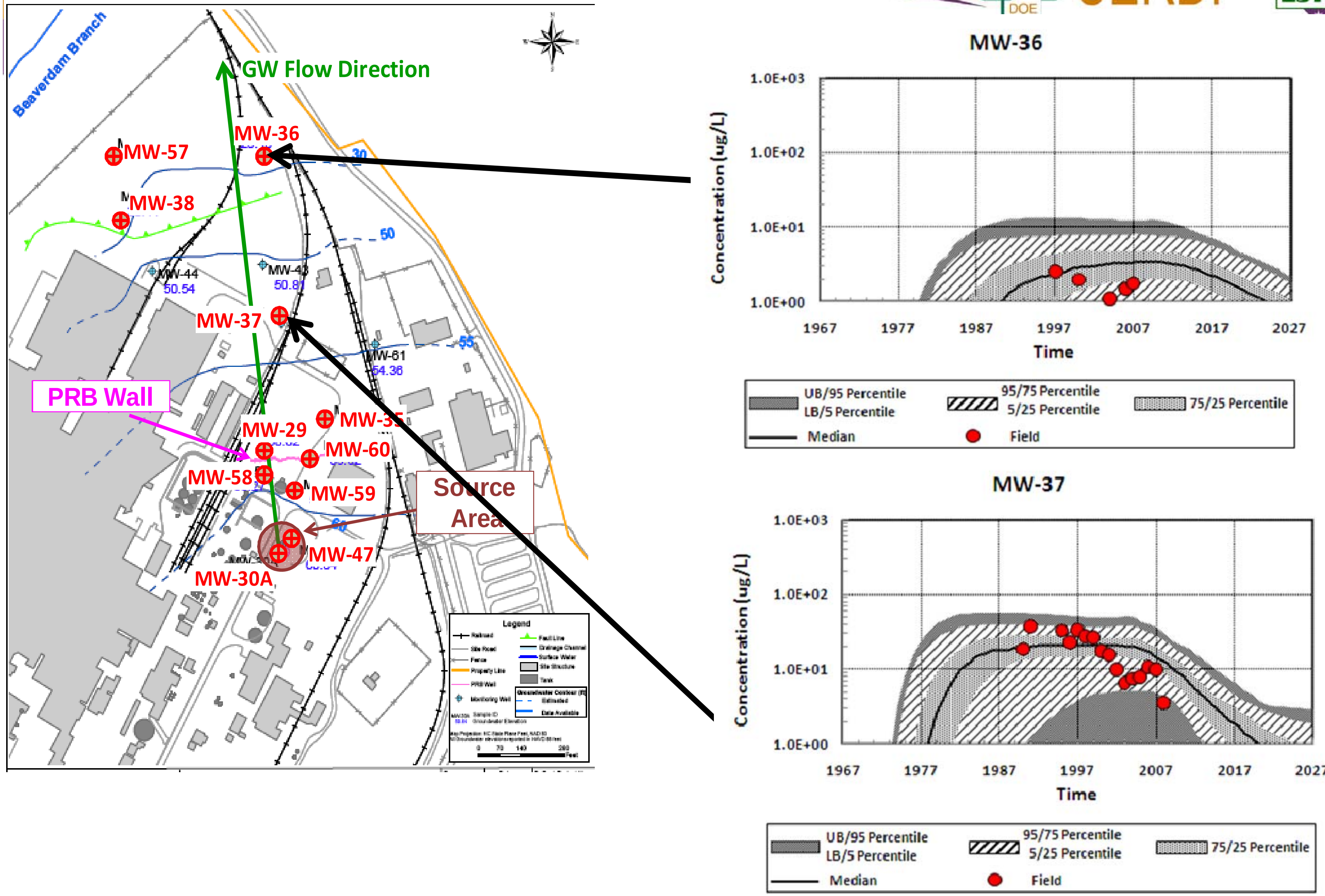

MW-59
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Concentration (ug/L)
1967
1977
1987
1997
2007
2017
2027
Time
UB/95 Percentile
LB/5 Percentile
95/75 Percentile
5/25 Percentile
75/25 Percentile
Median
Field







Well MW-29 is just downgradient of PRB wall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GW Flow Direction
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Source Area
60
MW-47
MW-30A
Legend
MW-36
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Concentration (ug/L)
1967
1977
1987
1997
2007
2017
2027
Time
UB/95 Percentile
LB/5 Percentile
95/75 Percentile
5/25 Percentile
75/25 Percentile
Median
Field
MW-37
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Concentration (ug/L)
1967
1977
1987
1997
2007
2017
2027
Time
UB/95 Percentile
LB/5 Percentile
95/75 Percentile
5/25 Percentile
75/25 Percentile
Median
Field

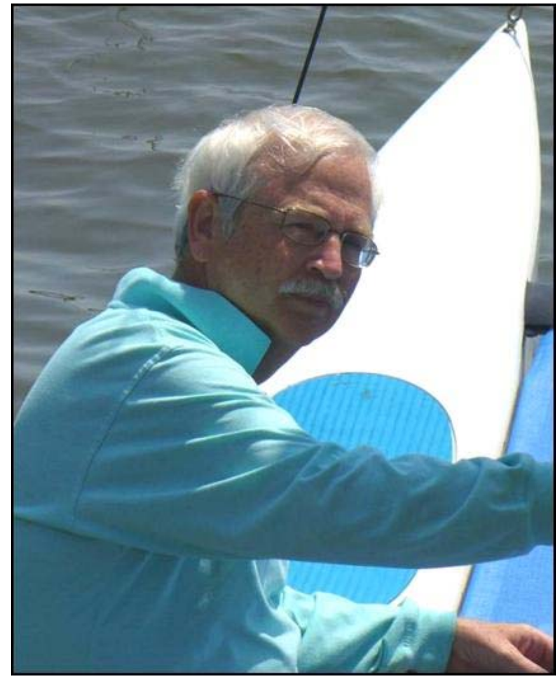
How to get Probabilistic REMChlor

- See handout.
- Download dll and player files from Clemson FTP site;
- Download GoldSim Player executable from GoldSim site (free)

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

Planning and Design of Emulsified Oil Injection Systems



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Aaron Weispfenning
Matthew Clayton
NC STATE UNIVERSITY

Thomas Simpkin
CH2MHILL

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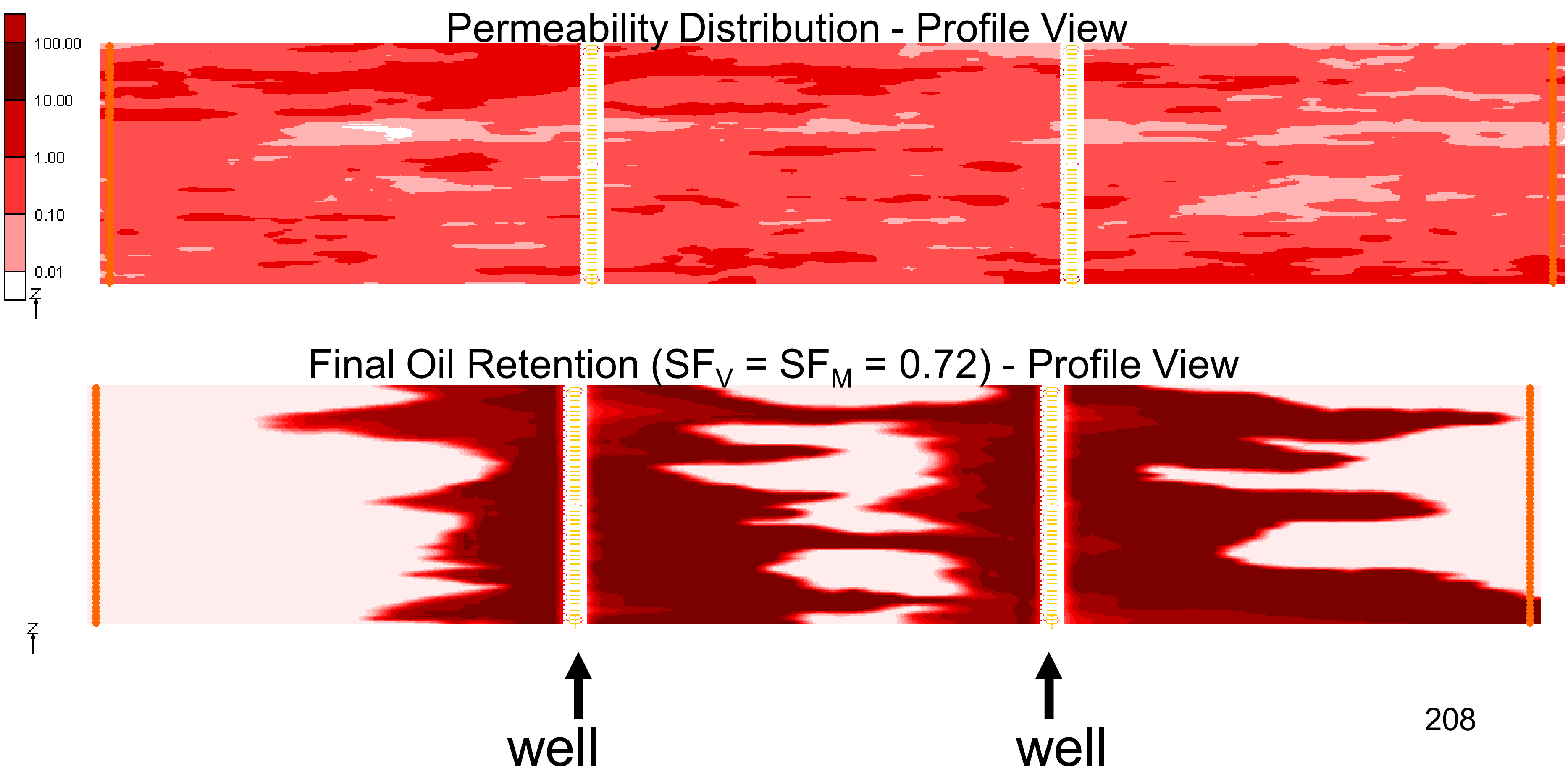
  - North Carolina State University
    (Robert Borden, Aaron Weispfenning, and Matt Clayton)
  - Solutions-IES (M. Tony Lieberman)
  - CH2M Hill (Tom Simpkin)
- Financial and technical support from ESTCP
- NCSU is not sponsoring or endorsing this presentation

Emulsified Oil Process

- Install temporary or permanent injection points
  - Grids or barriers
- Prepare and inject emulsion
- Inject water to distribute emulsion throughout treatment zone
- Oil droplets eventually stick to sediment surfaces
- Oil slowly ferments to H_2 and acetate
- H_2 and acetate drive anaerobic biodegradation processes
- Bioaugment if needed
- Monitor and wait

Numerical Modeling of Emulsified Oil Distribution

- MODFLOW/RT3D
- 3D heterogeneous aquifer



How to Improve Treatment?

- Good treatment requires good contact

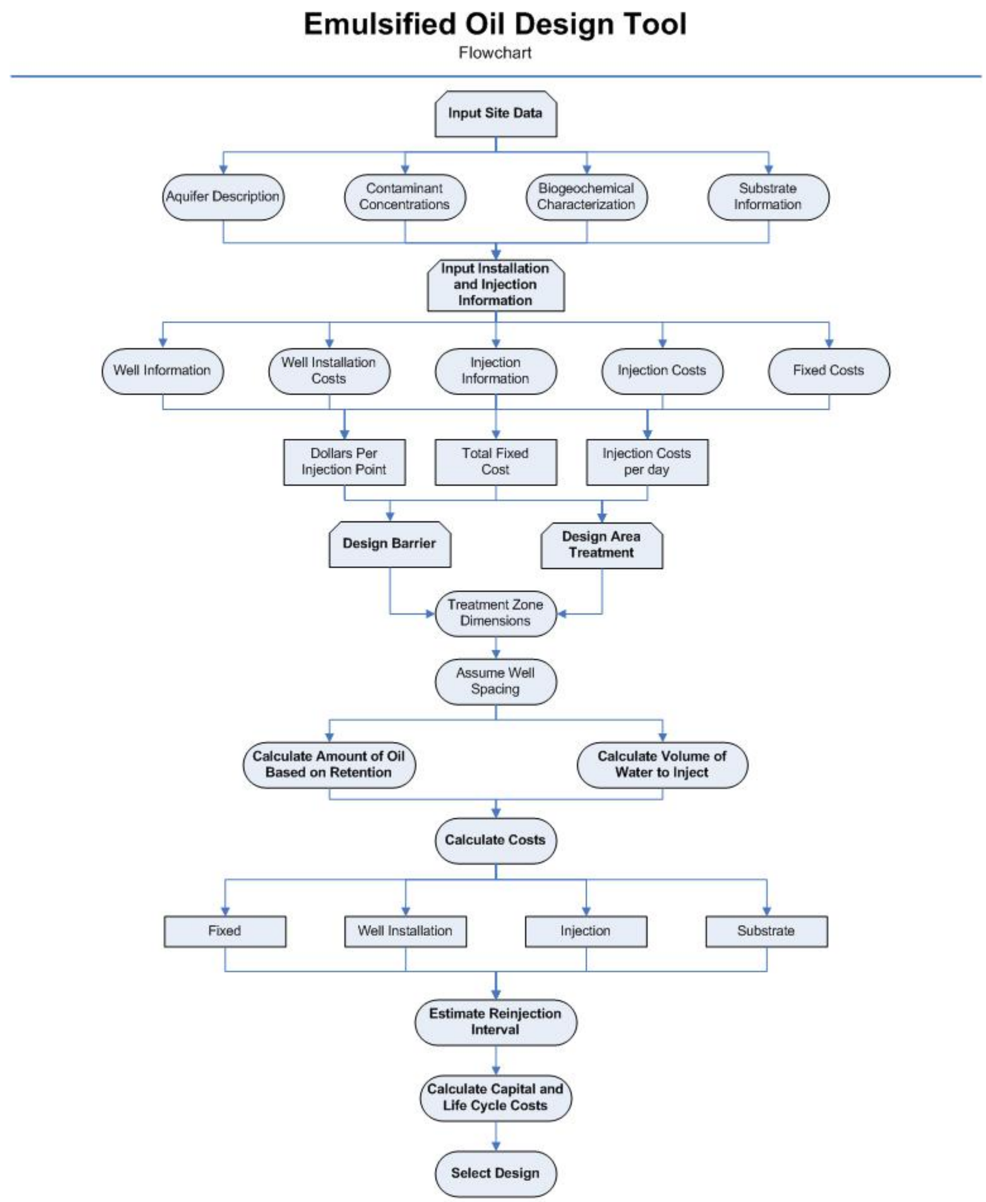
- How to improve contact
  - Inject more emulsified oil → more $$$
  - Inject more water to distribute oil → more $$$
  - Install more closely spaced wells → more $$$

- Problem: Which do I focus on?

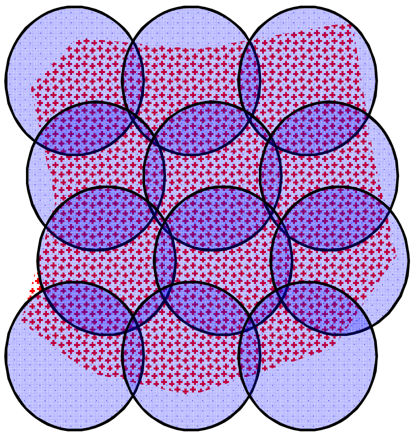
- Solution: ESTCP Project ER-0626
  Development of a Design Tool for Planning Aqueous Amendment Injection Systems

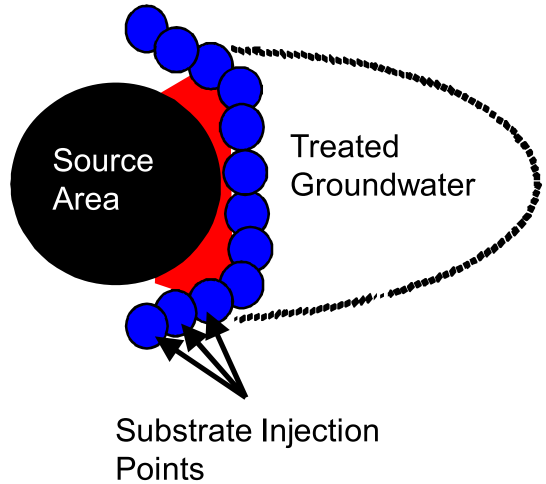
Injection System Design Tool – Injection Only

- Input
  - Site Data
    - Aquifer characteristics
    - Contaminants
    - Biogeochemical data
  - Costs
    - Fixed
    - Drilling
    - Substrate
    - Labor for injection
- Design Info
  - Treatment zone dimensions
  - Contact time
  - Design life
  - Scaling factors
- Output
  - Contact efficiency
  - Capital costs
  - Life cycle costs



Injection System Layout



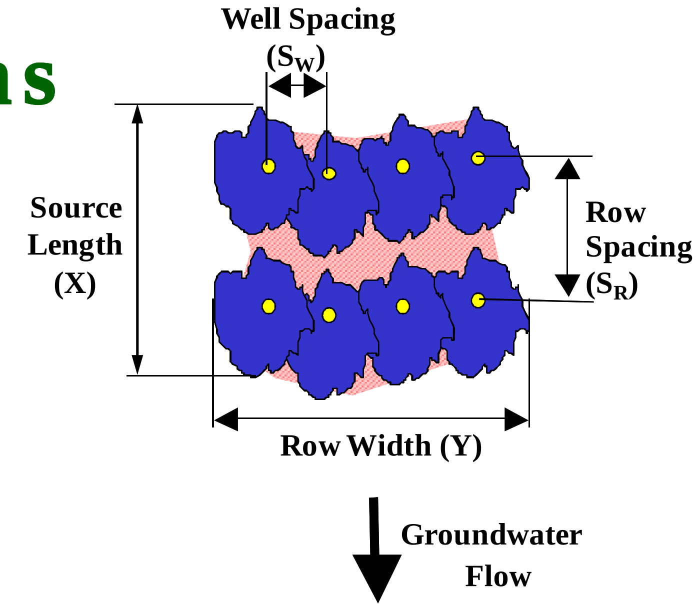


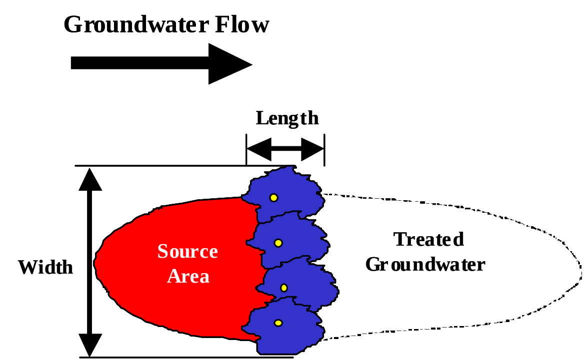
- Source Area
  - Grid of injection wells to 'saturate' source area
  - Requires
    - More wells
    - More substrate
  - Can displace contaminants
  - Treatment most effective in high K zones

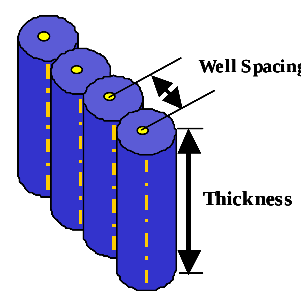
- Barrier(s)
  - Row of injection wells to intercept plume
  - Lower cost
    - Fewer wells
    - Less substrate
  - Lower potential for contaminant displacement
  - Does not eliminate source

Treatment Zone Dimensions

- Width perpendicular to GW flow (Y)
  - Source width
  - Barrier width
- Length parallel to GW flow (X)
  - Source length
  - In barriers, provide enough contact time
- Vertical Thickness (Z)
  - Use effective thickness when visibly different units are present
- Wells arranged in rows perpendicular to flow
  - Wider spacing between rows to allow for downgradient drift
- S_W = spacing of wells within a row
- S_R = spacing of rows
  - Design tool has an allowable ratio of S_R to S_W = 1:1 or 2:1
- Design tool will help select optimum S_W







How to Design an Injection System

- Fluid Volume = BTV * n_e * SF_V

  BTV = Base Treatment Volume

  n_e = Effective Porosity (dimensionless)

  SF_V = Volume Scaling Factor (dimensionless)

  SF_V typically 0.2 to 0.6 for area treatment

- Oil Requirement = OR_M * BTV * ϱ_B * SF_M

  OR_M = Maximum Oil Retention (lb oil / lb soil)

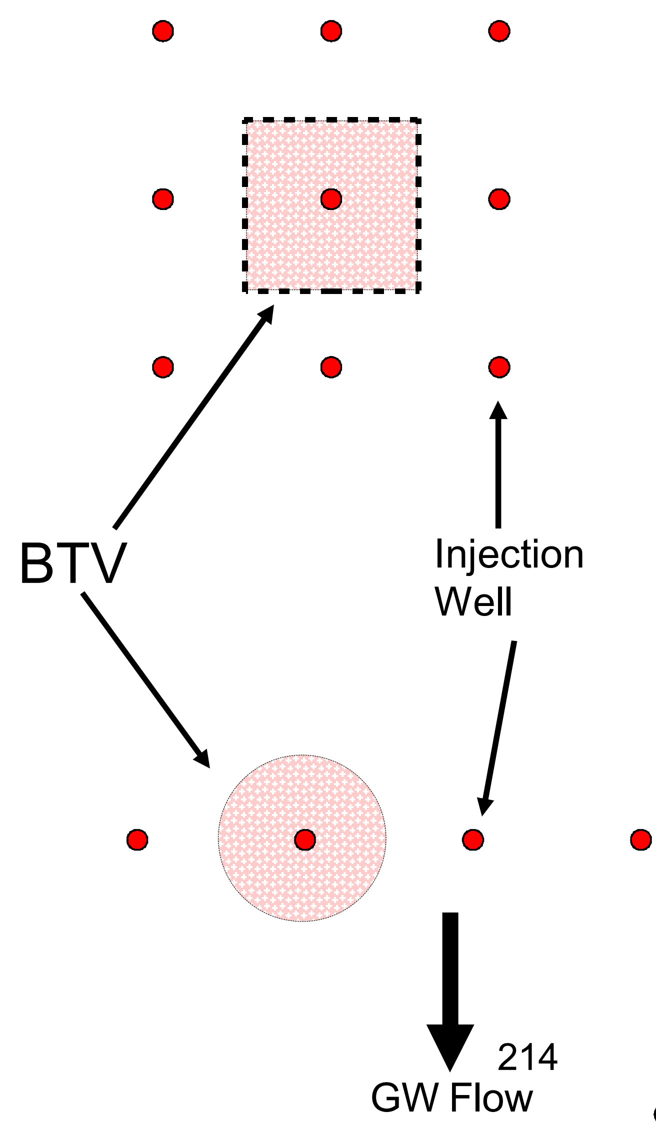
  ϱ_B = Soil Bulk density (lb/ft^3)

  SF_M = Mass Scaling Factor (dimensionless)

  SF_M typically 0.2 to 0.6 for area treatment

Base Treatment Volume (BTV)

- BTV = 'standard' volume around each well used to scale treatment quantities
- For Area Treatment
  BTV = volume of rectangular prism surrounding each well
  BTV = $S_W * S_R * Z$
- For Barrier Treatment
  BTV = volume of cylinder surrounding each well
  BTV = $\frac{1}{4} \pi S_W^2 * Z$



Oil Retention (OR) by Sediment

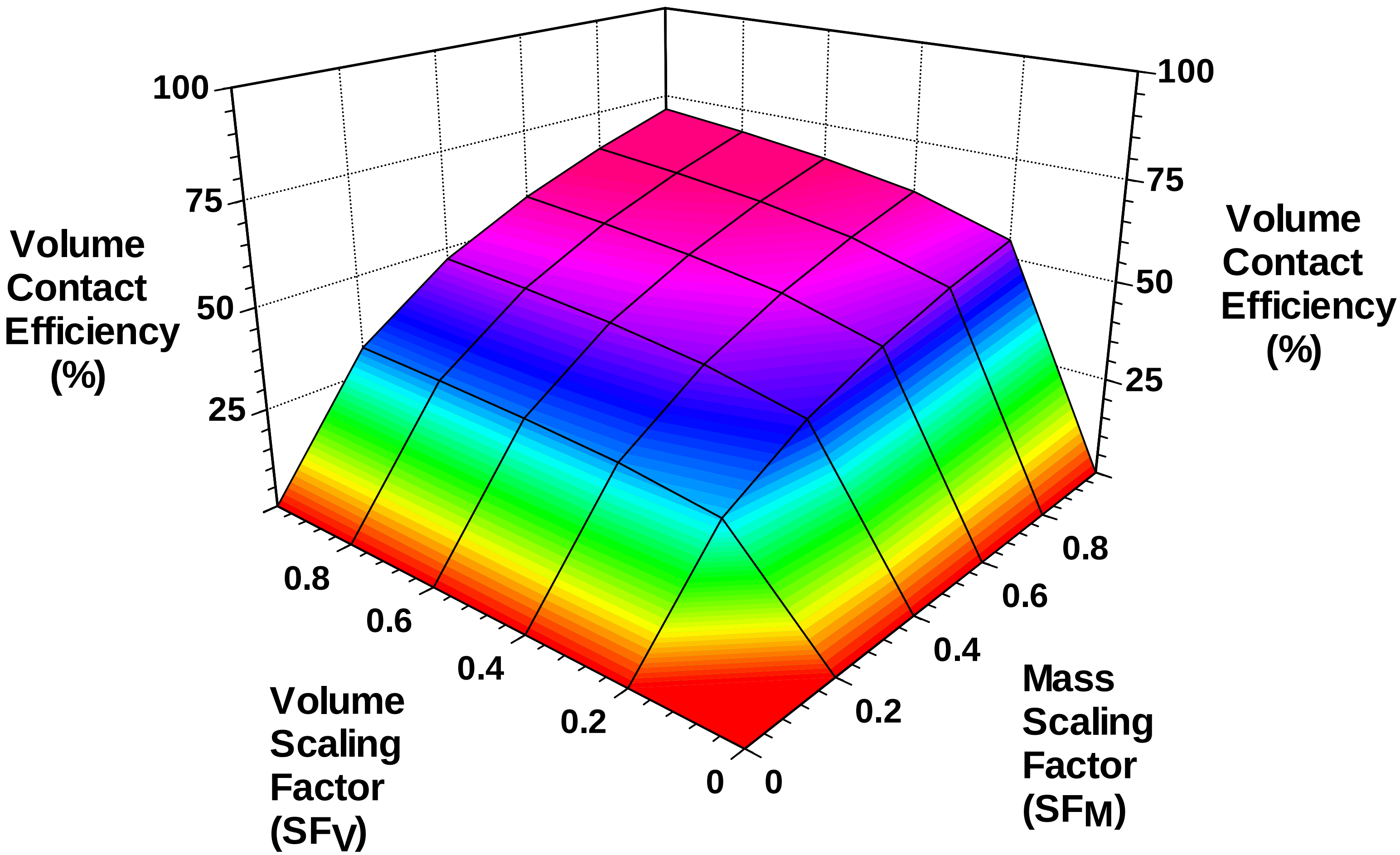
Oil retention is a function of

- Droplet size
  - Oil droplets should be smaller than sediment pores for easy transport
  - ~ 1 µm easily pass through most pores (30 - 100 µm)
- ‘Capacity’ of soil to hold oil droplets
  - Silts and clays have more charged sites → hold more oil
- Surfactant type
  - Non-ionics typically have lower sorption
  - Ionics have higher sorption (lecithin sorption is very high)
- Surface charge (zeta potential) of sediments and droplets
  - Most clays have a net negative charge
  - Negatively charged droplets will have lower retention

Maximum Oil Retention (OR_M)

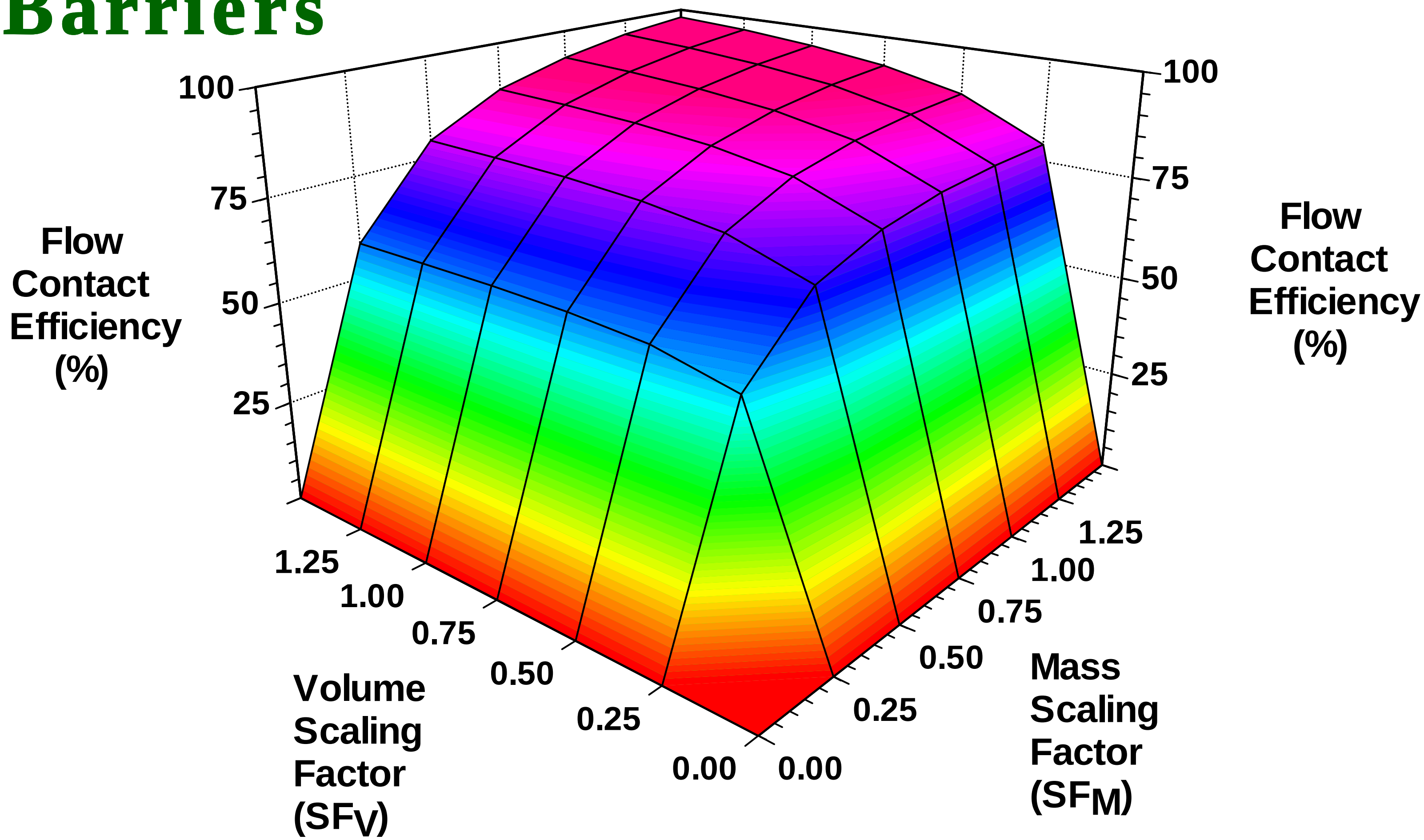
Aquifer Material	Emulsion	Test Condition	Maximum Retention (g/g)
Blended sand (7% Silt+Clay)	Homemade	Column	0.0054
Blended sand (9% Silt+Clay)	Homemade	Column	0.0061
Blended sand (12% Silt+Clay)	Homemade	Column	0.0095
Alluvium (clayey sand)	EOS®	Column	0.0037
Low K, weathered rock (sandy clay)	EOS®	Field	0.003 (estimated)
High K, gravelly sand	EOS®	Field	0.0004 (estimated)

Volume Contact Efficiency for Area Treatment
(Row Spacing = Well Spacing)



Clayton, M. H., and R. C. Borden, Numerical Modeling of Emulsified Oil Distribution in Heterogeneous Aquifers, Ground Water, 47(2): 246–258, 2009.

Flow Contact Efficiency for Barriers



Clayton, M. H., and R. C. Borden, Numerical Modeling of Emulsified Oil Distribution in Heterogeneous Aquifers, Ground Water, 47(2): 246–258, 2009.

Barrier Contact Time

- Contact time (C_t) between oil and contaminants
  - Provide 60 – 120 days for satisfactory chlorinated solvent removal
  - Use longer C_t for:
    - High sulfate loading
    - 'Unknown' high K layers that could cause short-circuiting through oil treated zone
    - High contaminant concentrations
    - High removal efficiency required
- Barrier length along flow direction (x) (length parallel to flow)

$$X = C_t * v$$

v = non-reactive transport velocity

How to Estimate Oil Reinjection Frequency

- Calculate oil required for biodegradation
  - Background Electron Acceptors
    - O_2, NO_3, SO_4
  - Contaminant to be treated
    - TCE, ClO_4, etc.
  - Organic carbon released to downgradient aquifer
    - Based on chemical composition of oil and microbiology
    - Typically assume average of 50-100 mg/L over project life for EOS®
  - Reduced compounds produced
    - Dissolved Fe, Mn, CH_4

- Oil Demand (D) is substrate consumed per volume of water that flows through each treatment row

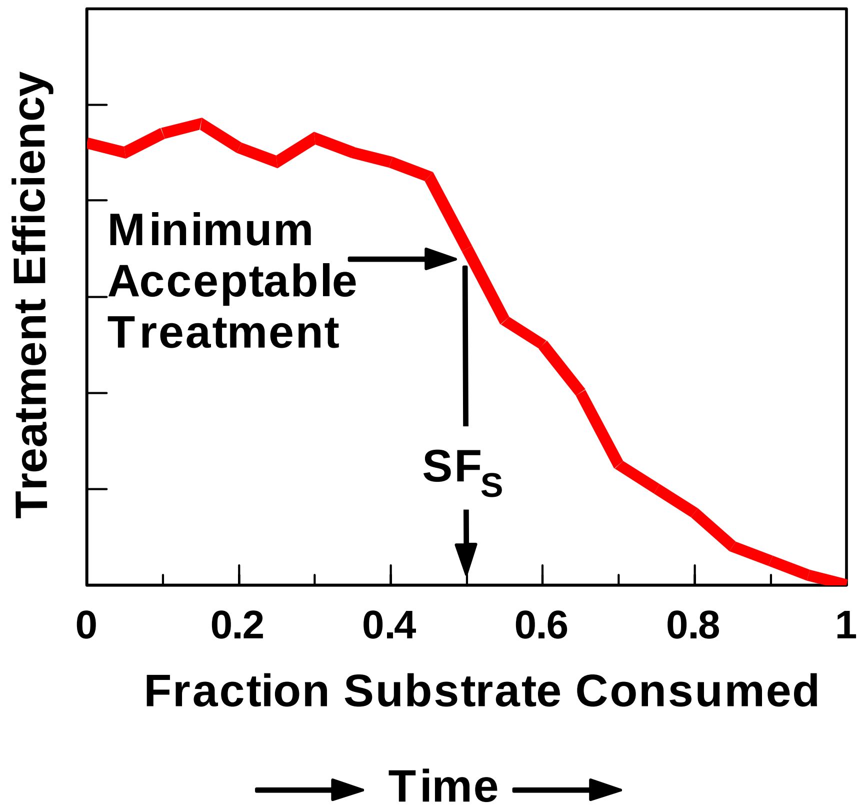
Treatment Performance in Barriers as Substrate is Consumed

Treatment efficiency

- maximum when excess substrate is present
- will drop as substrate is consumed

Substrate Scaling Factor (SF_S)

- SF_S = fraction of substrate consumed when treatment < acceptable
- $SF_S \rightarrow$ time to reinject
- SF_S typically varies from 0.3 to 0.6



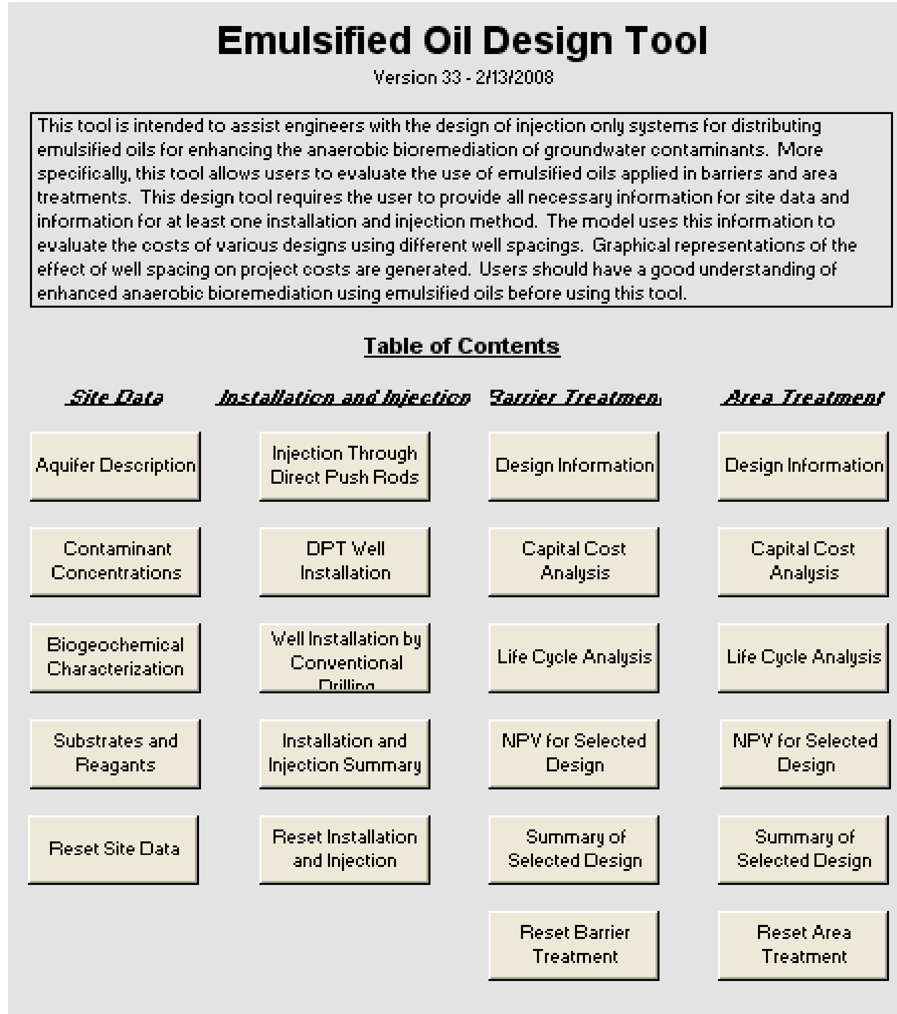
Determine Injection Frequency for Barriers

- Theoretical life of single injection (T)
  - T = Oil Injected / (D * Q)
  - Water Flux (Q) = Y * Z * K * i
    - Y= Width perpendicular to flow
    - Z = Effective treatment zone thickness
    - K = Hydraulic conductivity
    - i = Hydraulic gradient
  - D = Oil Demand (mg of oil / L of water)

- Reinjection Interval (RI) = T * SF_S
  - Design tool has maximum allowable period between reinjections that will over-ride calculation

Design Tool Table of Contents

- Four sections
- Click on button to navigate to a page
- Each page has a button to go forward, backward, or back to table of contents
- Reset buttons reset all pages within a section
- Start with Aquifer Description



Aquifer Description

- Enter information in the cells outlined in red
- White cells outlined in black are for additional information and do not need to be completed

Site Data - Aquifer Description

Information on the physical characteristics of the aquifer is entered on this page. This information will later be used to calculate injection volumes and costs for barrier and area treatments.

1 *Site Information*

a	Name	
b	Description (e.g., project number)	
c	Location	

2 *Hydraulic Characteristics*

a	Depth to water table		ft	0.00	m
b	Depth to top of injection zone		ft	0.00	m
c	Depth to bottom of injection zone		ft	0.00	m
d	Hydraulic Gradient		ft/ft	0	m/m
e	Hydraulic Conductivity		ft/day	0.00E+00	cm/s
f	Estimated Total Porosity				
g	Estimated Effective Porosity				
h	Seepage Velocity	#DIV/0!	ft/day	#DIV/0!	cm/s
		#DIV/0!	ft/yr	#DIV/0!	m/yr

3 *Soil Characteristics*

a	Description of Soil Lithology				
b	Bulk Density		lbs/ft^3	0.0	g/cm^3
c	Maximum Oil Retention by soil (see Table 4.2 in design manual). This value has a critical impact on cost and treatment performance.		lbs oil/lbs soil	0	kg oil/kg soil

Return to Table of Contents | Go Back to Previous Page (Introduction) | Go Forward to Next Page (Contaminant Concentrations)

Contaminant / Biogeochemical Characterization

- Enter concentrations for contaminants and background electron acceptors
- Additional contaminants can be included by specifying the concentration, molecular weight, and the electron equivalents per mole

Data - Contaminant Concentrations

Information on the concentration of common contaminants are entered on this page. This information is used to calculate the number of electron equivalents (e- equiv) required to biodegrade these contaminants. Several of the more common contaminants are listed below along with their molecular weight (MW) and e- equiv/mole. Blank cells in rows m, n, and o allow the user to enter information on additional contaminants. For these additional contaminants, the user must enter the contaminant concentration, MW and e- equiv/mole.

		µg/L	MW (g/mole)	e- equiv/ mole	e- equiv demand (e- equiv/L)
a	Tetrachloroethene (PCE), C_2Cl_4		165.8	8	
b	Trichloroethene (TCE), C_2HCl_3		131.4	6	
c	cis-1,2-dichloroethene (c-DCE), $C_2H_2Cl_2$		96.9	4	
d	Vinyl Chloride (VC), C_2H_3Cl		62.5	2	
e	Carbon tetrachloride, CCl_4		153.8	8	
f	Chloroform, $CHCl_3$		119.4	6	
g	*sym*-tetrachloroethane, $C_2H_2Cl_4$		167.8	8	
h	1,1,1-Trichloroethane (TCA), CH_3CCl_3		133.4	6	
i	1,1-Dichloroethane (DCA), CH_3CHCl_2		99.0	4	
j	Chloroethane, C_2H_5Cl		64.9	2	
k	Perchlorate, ClO_4^-		99.4	8	
l	Hexavalent Chromium, Cr[VI]		52.0	3	
m					
n					
o					
p	e- equiv demand from contaminant concentrations	0.00E+00	e- equiv/L		

Data - Biogeochemical Characterization

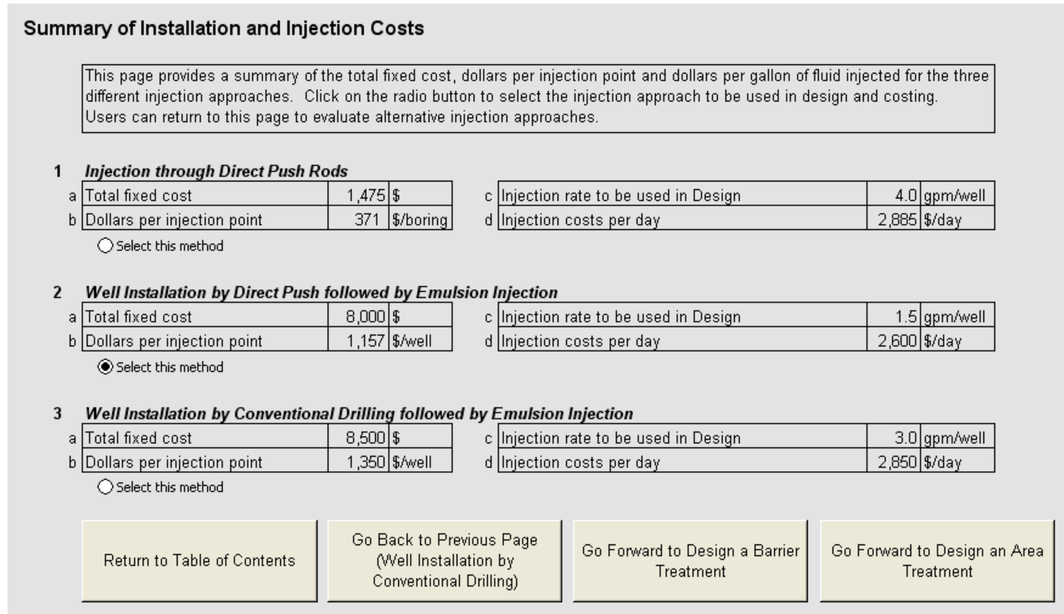
Information on the concentration of background electron acceptors is entered on this page. This information is used to calculate the number of electron equivalents (e- equiv) required to deplete these materials. The total e- equivalent is then calculated from the contaminant demand and the background electron acceptor demand. This value is later used to calculate the annual substrate demand.

		mg/L or mg/Kg	MW (g/mole)	e- equiv/ mole	e- equiv demand (e- equiv/L)
a	Background Dissolved Oxygen (mg/L)		32.0	4	
b	Background Nitrate (mg/L as N)		14.0	5	
c	Background Sulfate (mg/L)		96.1	8	
d	Estimated methane produced (mg/L)		16.0	8	
e	Soil Manganese Content (mg/Kg) (not used in calculation)				
f	Estimated Mn^{2+} produced (mg/L)		54.9	2	
g	Soil Iron Content (mg/Kg) (not used in calculation)				
h	Estimated Fe^{2+} produced (mg/L)		55.8	1	
i	pH (not used in calculation)				
j	Alkalinity (mg/L) (not used in calculation)				
k	e- equiv demand from biogeochemical characterizeation	0.00E+00	e- equiv/L		

Total e- equiv demand (e- equiv/L)
0.00E+00

Well Installation Method

- Approach assumes temporary or permanent wells are installed using direct push equipment
- Multiple wells are manifolded together for emulsion injection
- Select the method on the Installation and Injection Summary page



Summary of Installation and Injection Costs

This page provides a summary of the total fixed cost, dollars per injection point and dollars per gallon of fluid injected for the three different injection approaches. Click on the radio button to select the injection approach to be used in design and costing. Users can return to this page to evaluate alternative injection approaches.

1 *Injection through Direct Push Rods*

a	Total fixed cost	1,475	$	c	Injection rate to be used in Design	4.0	gpm/well
b	Dollars per injection point	371	$/boring	d	Injection costs per day	2,885	$/day

○ Select this method

2 *Well Installation by Direct Push followed by Emulsion Injection*

a	Total fixed cost	8,000	$	c	Injection rate to be used in Design	1.5	gpm/well
b	Dollars per injection point	1,157	$/well	d	Injection costs per day	2,600	$/day

◉ Select this method

3 *Well Installation by Conventional Drilling followed by Emulsion Injection*

a	Total fixed cost	8,500	$	c	Injection rate to be used in Design	3.0	gpm/well
b	Dollars per injection point	1,350	$/well	d	Injection costs per day	2,850	$/day

○ Select this method

Return to Table of Contents | Go Back to Previous Page (Well Installation by Conventional Drilling) | Go Forward to Design a Barrier Treatment | Go Forward to Design an Area Treatment

Results of the analysis are broken into:

- Total fixed cost
- Dollars per injection point
- Injection rate
- Injection costs per day

Barrier Design Information

- User enters information on:
  - Treatment zone dimensions
  - Treatment zone contact time
  - Targeted carbon released
  - Design life
  - Mass, volume and substrate scaling factors
- Model calculates expected contact efficiency

Single Permeable Reactive Barrier - Design Information

Design criteria for installation of a single permeable reactive barrier is entered on this page. This criteria is later used to determine material quantities and estimate costs for a variety of design alternatives.

1 *Treatment Zone Dimensions*

a	Width (perpendicular to groundwater flow)		ft	0.00	m
b	Effective Treatment Zone Thickness	0	ft	0.00	m
i.	Top of Treatment Zone	0	ft	0.00	m
ii.	Bottom of Treatment Zone	0	ft	0.00	m
c	Seepage Velocity	#DIV/0!	ft/day	#DIV/0!	cm/s
d	Groundwater Flux through Treatment Zone	#DIV/0!	gal/yr	#DIV/0!	L/yr

2 *Treatment Zone Contact Time*

A minimum contact time of 2 to 4 months is typically required for effective treatment of chlorinated solvents in emulsified oil barriers. Longer contact times may be needed for difficult to degrade contaminants, with higher contaminant concentrations, and/or high concentrations of competing electron acceptors. Shorter contact times may be acceptable for easily treated contaminants (e.g. nitrate or perchlorate) or when only partial treatment is required.

a	Minimum Allowable Contact time		days		
b	Minimum Allowable Contact length		ft	0.00	m
c	Minimum length to be used in design	#DIV/0!	ft	#DIV/0!	m

3 *Targeted Carbon Released*

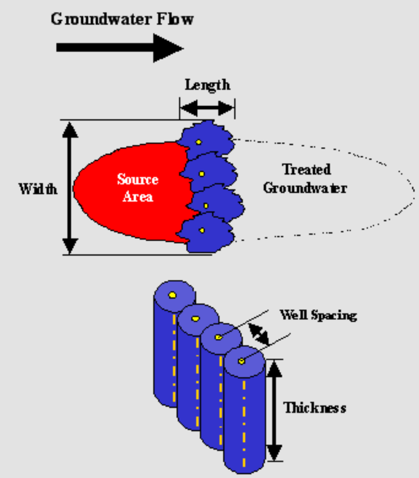
Emulsified oil barriers release dissolved organic carbon (DOC) over the life of the barrier. This DOC released is in excess of that required for contaminant biodegradation and consumption of competing electron acceptors. Field monitoring data indicates that DOC released from barriers declines from hundreds mg/L shortly after emulsion injection to tens of mg/L near the end of the operating life. Long-term average DOC concentrations are typically in the range of 40 - 100 mg/L.

a	Average Amount of DOC Released		mg/L		
b	DOC Released per year	#DIV/0!	lb	#DIV/0!	kg

4 *Design Life*

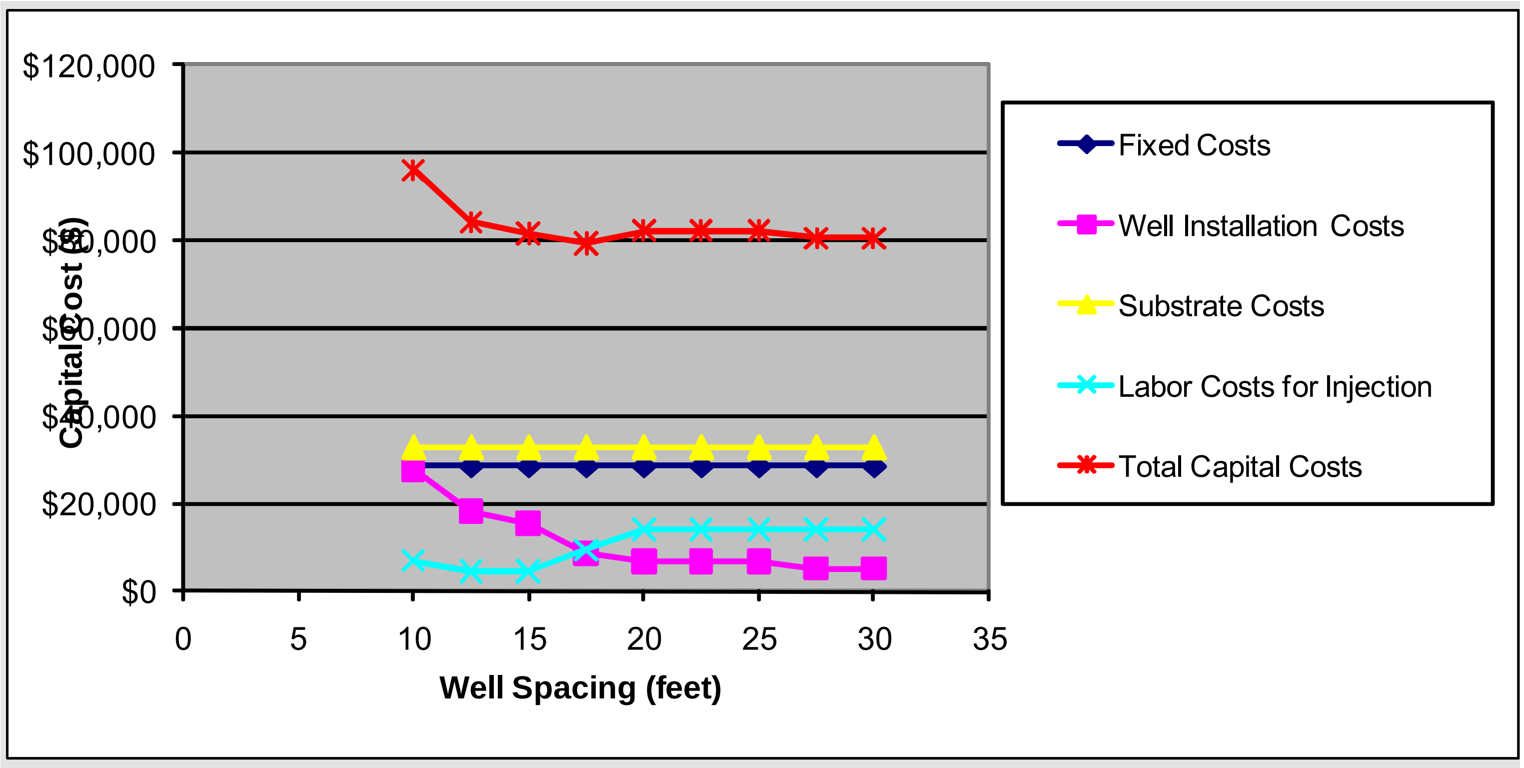
The design tool estimates reinjection frequency based on amount of substrate injected, the annual substrate consumption rate, and fraction of initial substrate consumed when when treatment performance declines. However, users may specify a maximum time between reinjections. The design tool will then use the smaller of these two values. Life cycle costs are calculated based on the reinjection frequency and other ongoing costs (monitoring, etc.)

a	Total Project Life (Max of 30 years)		years
b	Subtrate Scaling Fator (typically 0.3 to 0.6)		
c	Maximum Time between Reinjections		years



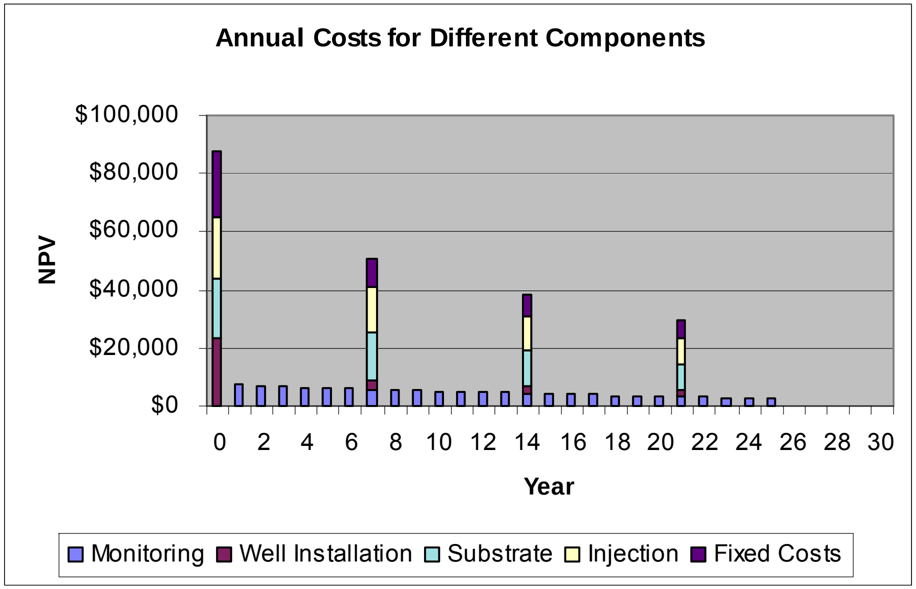
Capital Cost Analysis

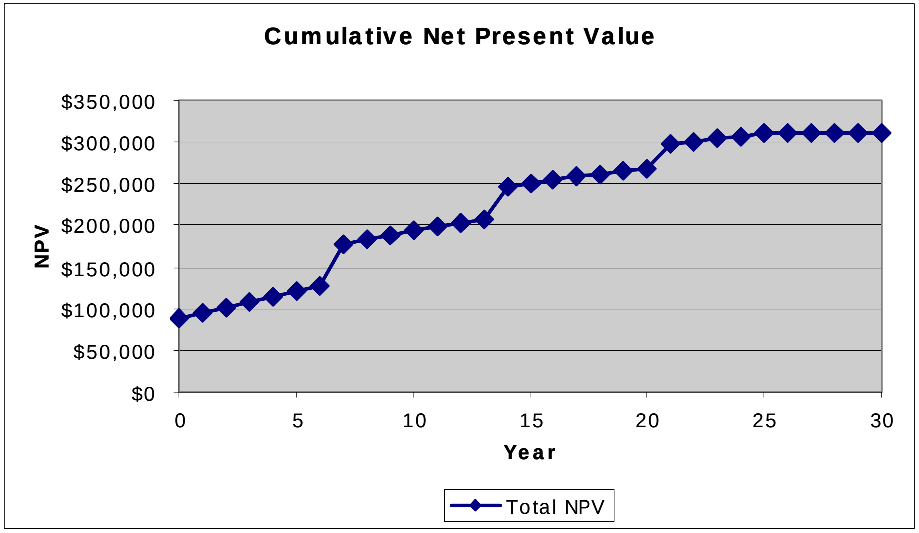
- Enter minimum well spacing and incremental increase
- Enter planning and engineering costs
- Look at capital cost vs well spacing



Life Cycle Cost Analysis

- Enter information on:
  - Annual interest rate
  - Engineering costs for each future event
  - Well replacement / rehabilitation for future injections
  - Annual monitoring and reporting costs
  - Results are presented as lifetime Net Present Value (NPV) vs well spacing
  - Select a design (15 ft) to see additional information





Print Out Design Summary

Area Treatment Using a Series of Barriers - Selected Design

This sheet shows a summary of the selected design that can be saved or printed before looking at alternative designs.

1	***Site Information***				
a	Name	Example Site			
b	Description (e.g., project number)	AFB			
c	Location	Florida			
d	Maximum Oil Retention	0.009	lbs oil/lbs soil		
2	***Treatment Design Criteria***				
a	Reinjection Interval	4	years		
b	Timeframe in which all groundwater in targeted area should theoretically flush through active treatment zones.	8	years		
3	***Well Layout***				
a	Well Spacing	13	ft	3.81	m
b	Number of Wells per Row	3	wells/row		
c	Row Spacing	12.5	ft	3.81	m
d	Number of Rows	7	rows		
e	Total Number of Wells	21	wells		
4	***Logistics for Each Injection Event***				
a	Total Mass of Oil Injected	5,891	lbs	2,672	kg
b	Total Injection Volume	9,425	gallons	35,679	L
c	Total Injection Volume per well	449	gal/well	1,699	L/well
d	Estimated Injection Rate	1.0	gpm/well		
e	Number of wells injected simultaneously	10	wells		
5	***Costs for Initial Installation and Injection***				
a	Fixed Costs (planning and installation)	$28,570			
b	Well Installation Costs	$18,200			
c	Injection Costs	$7,050			
d	Substrate Costs	$32,725			
e	Total Installation and Injection Costs	$86,545			
6	***Costs for Future Injection Events***				
a	Fixed Costs (engineering and installation)	$13,570			
b	Well Rehabilitation and/or Installation Costs	$4,550			
c	Labor Cost for Injection	$7,050			
d	Substrate Costs	$32,725			
e	Total Installation and Injection Costs	$57,895			
7	***Total Life Cycle Costs***				
a	Annual Interest Rate	5%			
b	Monitoring and Reporting	$64,632			
c	Total Injection Costs (fixed, well installation, labor for injection, and substrate)	$173,361			
d	Project Life NPV	$237,993			
8	***Design Parameters***				
a	Volume Scaling Factor	0.5			
b	Mass Scaling Factor	0.5			
c	Estimated Contact Efficiency for Injection	40%	to	54%	

Additional Resources

- Software Download
  - http://docs.serdp-estcp.org/ (search for Design Tool)
  - http://www4.ncsu.edu/~rcborden/Design_Tool.html
- Manual
  - Emulsified Oil Design Tool USERS MANUAL
  - Tutorial included in Manual Appendix
- Websites
  - SERDP/ESTCP (www.serdp-estcp .org)
    - A Treatability Test for Evaluating the Potential Applicability of the Reductive Anaerobic Biological In Situ Treatment Technology to Remediate Chloroethenes"
    - "Protocol for Enhanced In Situ Bioremediation Using Emulsified Edible Oil"
  - AFCEE (http://www.afcee.brooks.af.mil/products/techtrans/)
    - "Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents"
    - "Protocol for In Situ Bioremediation of Chlorinated Solvents Using Edible Oil"

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:20 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
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Planning and Design of Permanganate Injection Systems

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(rcborden@eos.ncsu.edu)

M. Tony Lieberman — Solutions-IES Industrial & Environmental Services

Ki Young Cha — NC STATE UNIVERSITY

Thomas Simpkin — CH2MHILL

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    - Robert Borden
    - Ki Young Cha
  - Solutions-IES
    - M. Tony Lieberman
  - CH2M Hill
    - Tom Simpkin
- Financial and technical support from ESTCP
- NCSU is not sponsoring or endorsing this presentation

ISCO using MnO_4

- Target Contaminants
  - Chlorinated Ethenes (PCE, TCE, DCE, VC)
  - RDX, HMX, TNT
- Not Effective for
  - Chlorinated ethanes (e.g., 1,1,1-TCA)
  - Carbon tetrachloride
  - Benzene, MTBE
- Injection Procedure
  - Install injection points
  - Prepare MnO_4 solution
  - Inject water to distribute MnO_4 solution throughout treatment zone
- MnO_4 is consumed by
  - Natural Oxidant Demand (NOD)
  - Target contaminant

$NaMnO_4$ feed system.

automatic $KMnO_4$ feed system

What is the Secret to making ISCO Work?

"Success is achieved by having enough oxidant in contact with the contaminant for a long enough period of time to react effectively"

ISCO Technology Practices Workshop
Colorado School of Mines, March 2007

- Design Tool Performance Criteria
  - Reagent distributed throughout target zone
  - MnO_4 concentration > _____ mg/L after ____ days
    - Target MnO_4 Concentration ~ 100 to 1000 mg/L
    - Target contact time ~ 10 to 100 days

Permanganate Design Tool Development

- Develop reaction kinetics to simulate MnO_4 consumption by NOD
- Implement model as:
  - RT3D
  - simple spreadsheet model (CDISCO)
- RT3D sensitivity analysis
  - 3-D heterogeneous aquifer
  - Range of injection volumes, MnO_4 loading and model parameters
- Use RT3D results to 'calibrate' CDISCO spreadsheet model

Modeling Approach

- Standard Advection – Dispersion Equations for Contaminant (C) and MnO_4 (M) transport

$$\frac{1}{R}\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i C\right) - F(C,M)$$

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial M}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i M\right) - F(C,M,N_I,N_S)$$

- Reaction Kinetics
  - Instantaneous reaction between C and M
  - Instantaneous reaction between M and NOD_I
  - 2nd Order reaction between M and NOD_S (N_S)

$$\frac{dM}{dt} = -K_S M N_S \rho_B / n$$

- Equations coded into
  - RT3D reaction module
  - Spreadsheet as series of CSTRs

- Model assumes No NAPL present

RT3D Simulations

Simulate small part of large injection grid

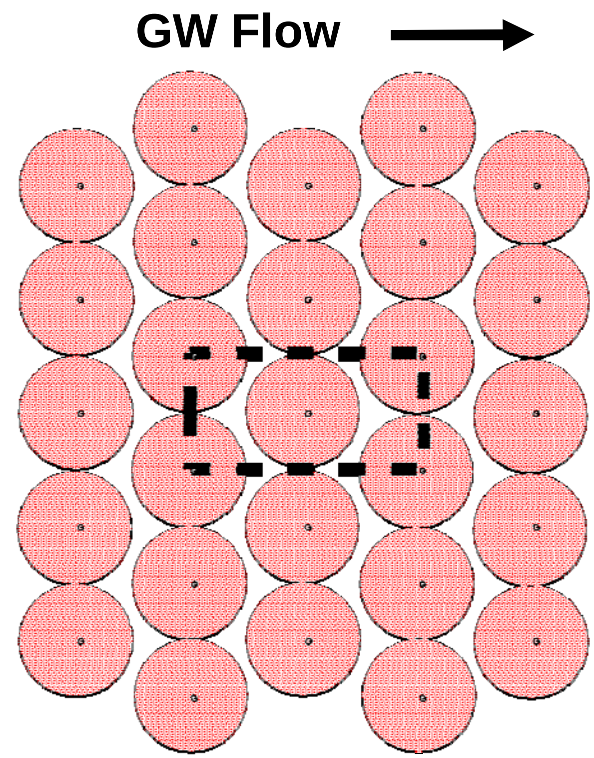
3-D Heterogeneous K distribution

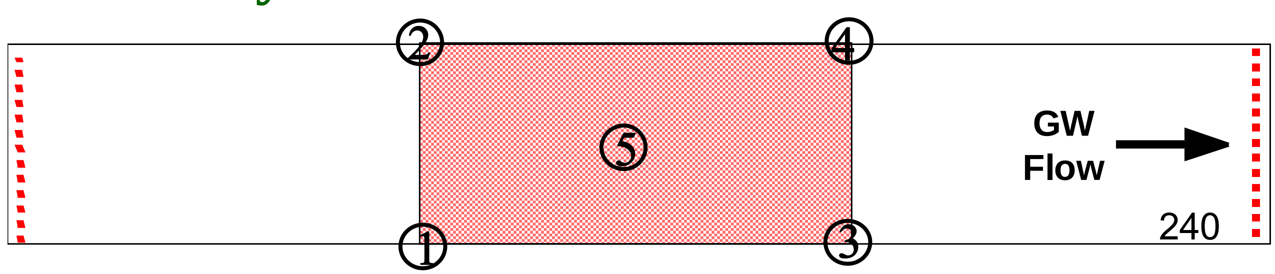
- Low, medium and high heterogeneity

Vary

- Mass of MnO_4 injected
- Volume of water injected
- Well spacing
- Injection sequence
- NOD kinetic parameters

Examine contact efficiency in target zone

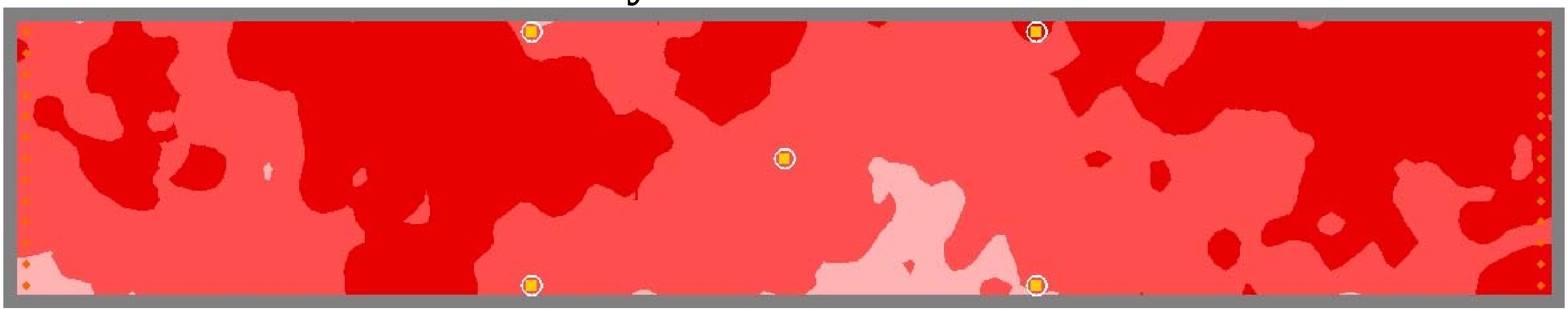




Typical Simulation Results for Stochastic Permeability Distribution - 'Medium Heterogeneity'

SERDP ESTCP

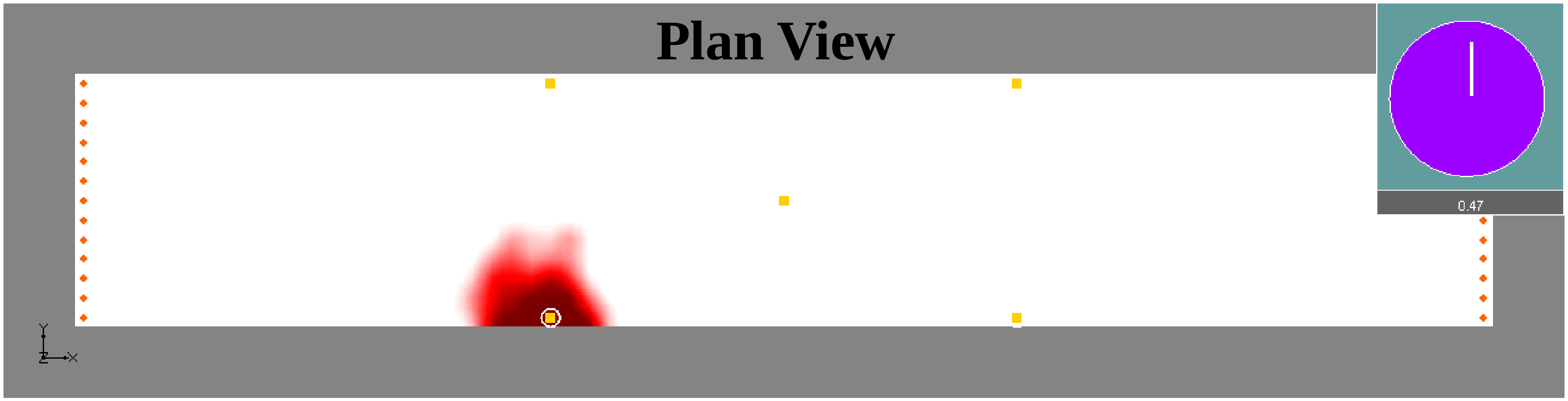
Permeability Distribution - Plan View

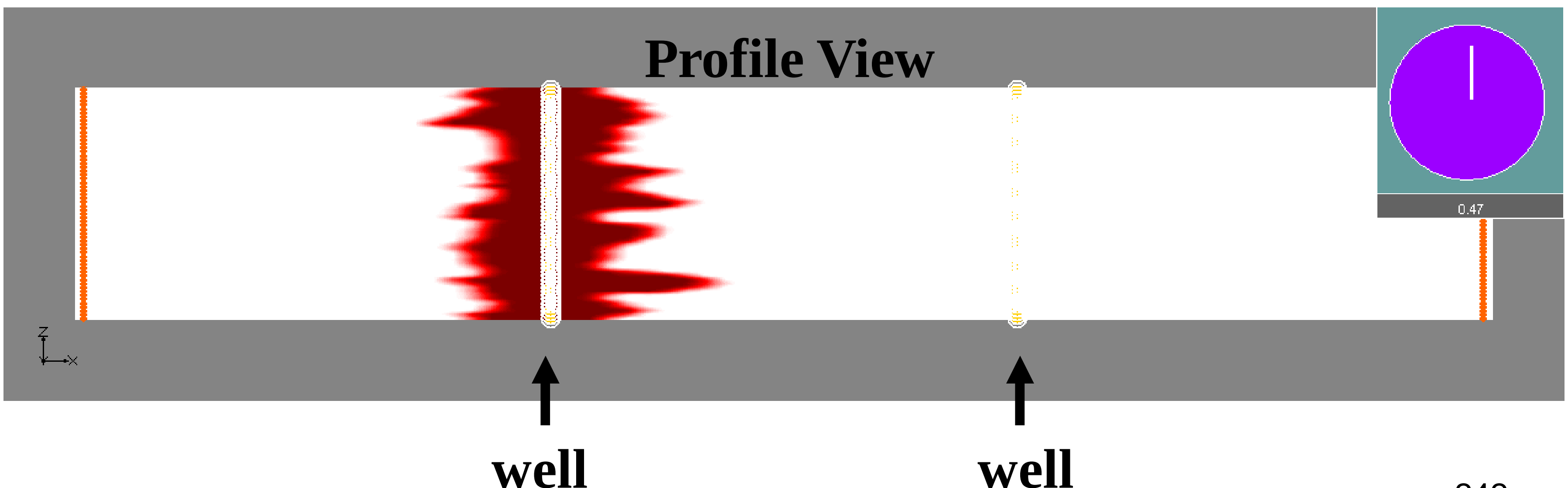


Permeability Distribution - Profile View

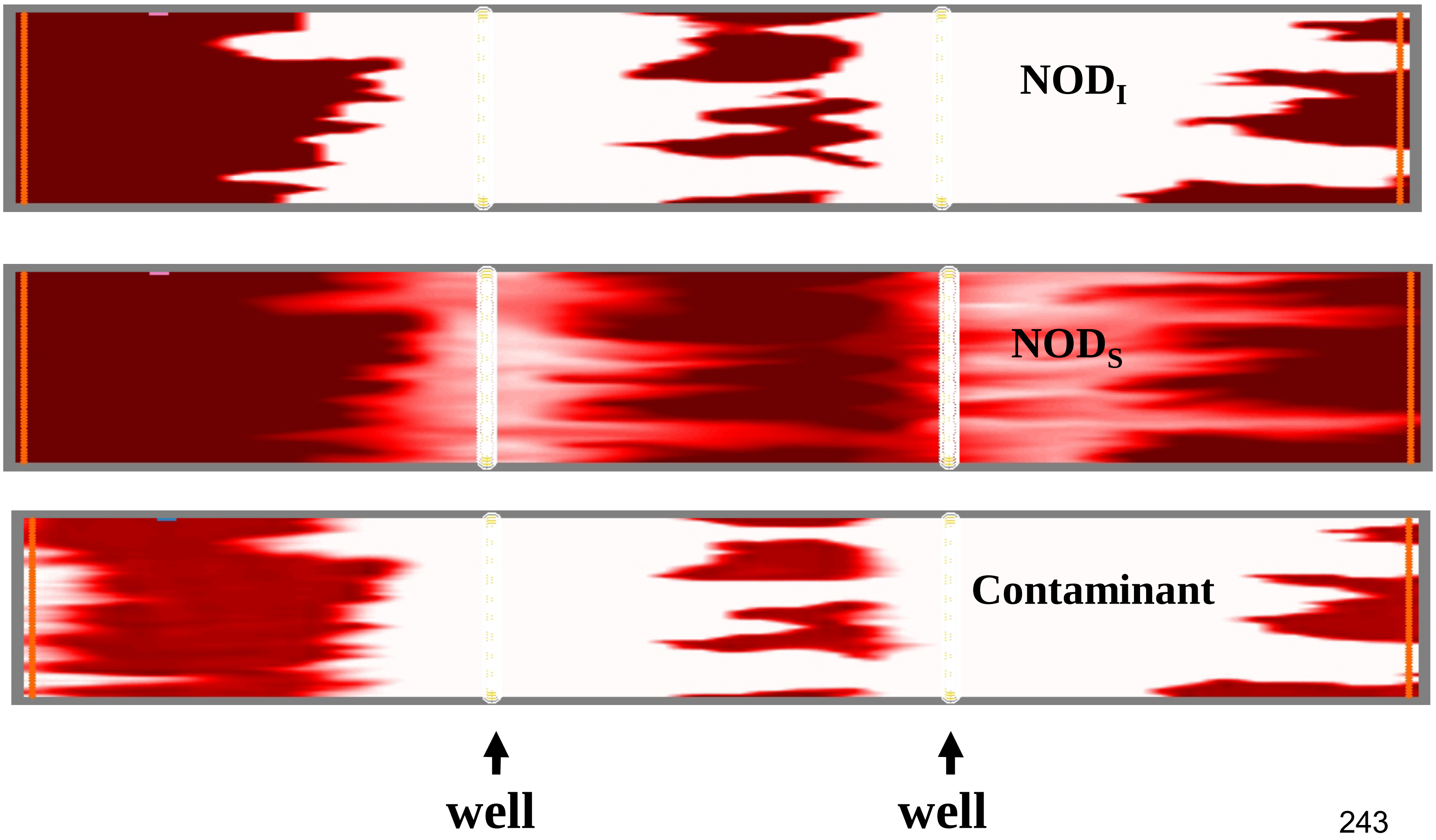
well well

Simulated MnO_4 Distribution



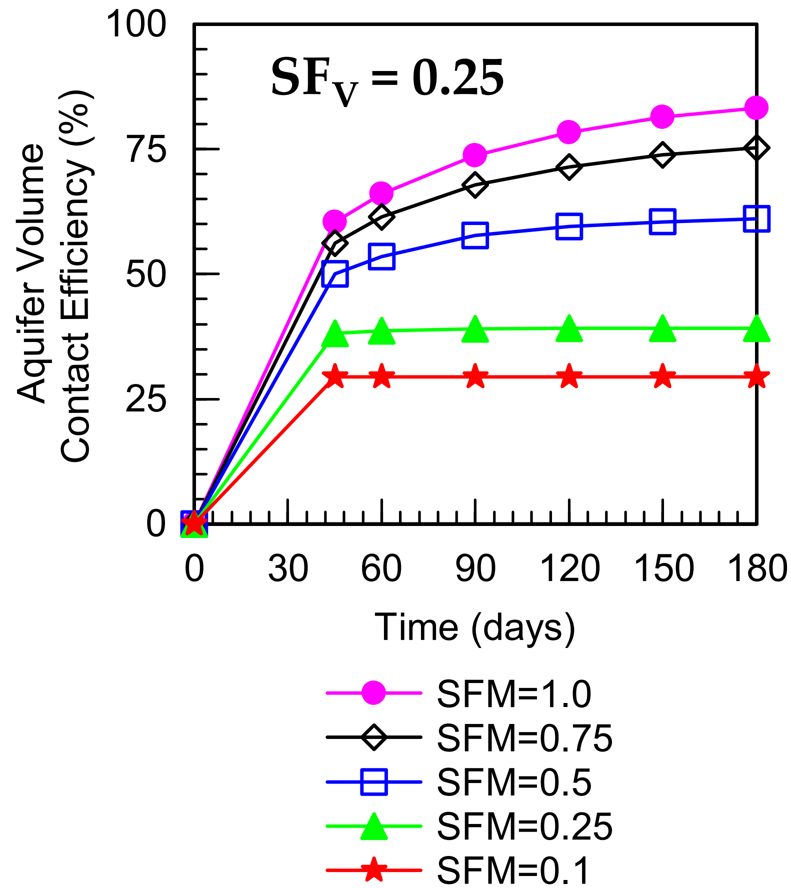


Simulation Results –
Profile View – 180 Days after Injection



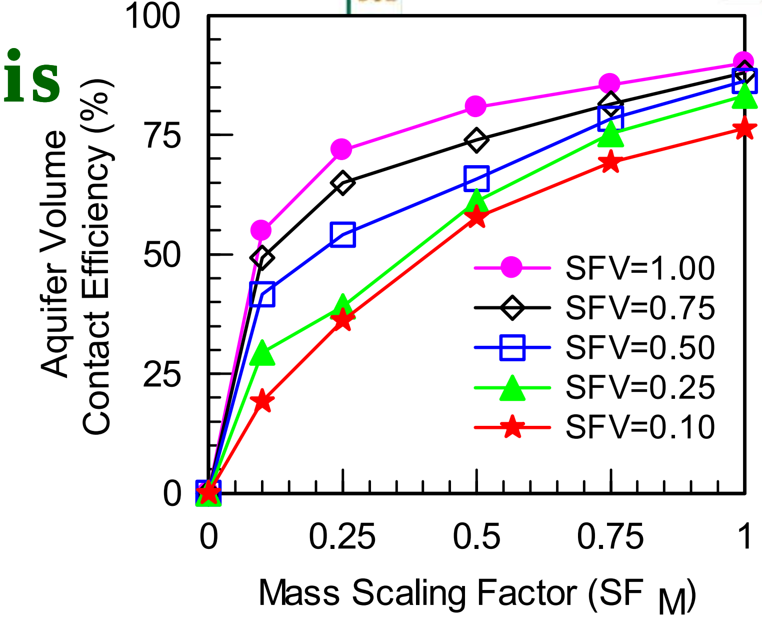
RT3D Sensitivity Analysis

- Design Parameters
  - Mass scaling factor (SF_M)
    $SF_M = MnO_4$ applied / ultimate demand
  - Volume scaling factor (SF_V)
    SF_V = Volume water / pore volume
- Performance Measure
  - Aquifer Volume Contact Efficiency (E_V)
- Results
  - E_V increase with time for large SF_M
    - Downgradient drift of MnO_4
    - Diffusion into low K zones
  - E_V at 180 days will be used as primary performance measure

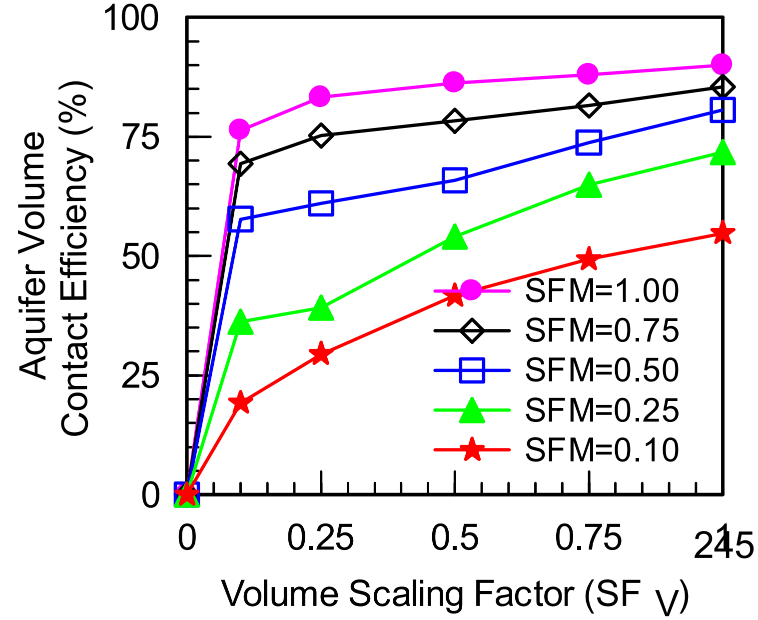


RT3D Sensitivity Analysis

- Effect of MnO_4 Mass Injected
  - Increasing SF_M (more MnO_4) increases contact efficiency
  - Caution: too much MnO_4 can cause downgradient release of MnO_4

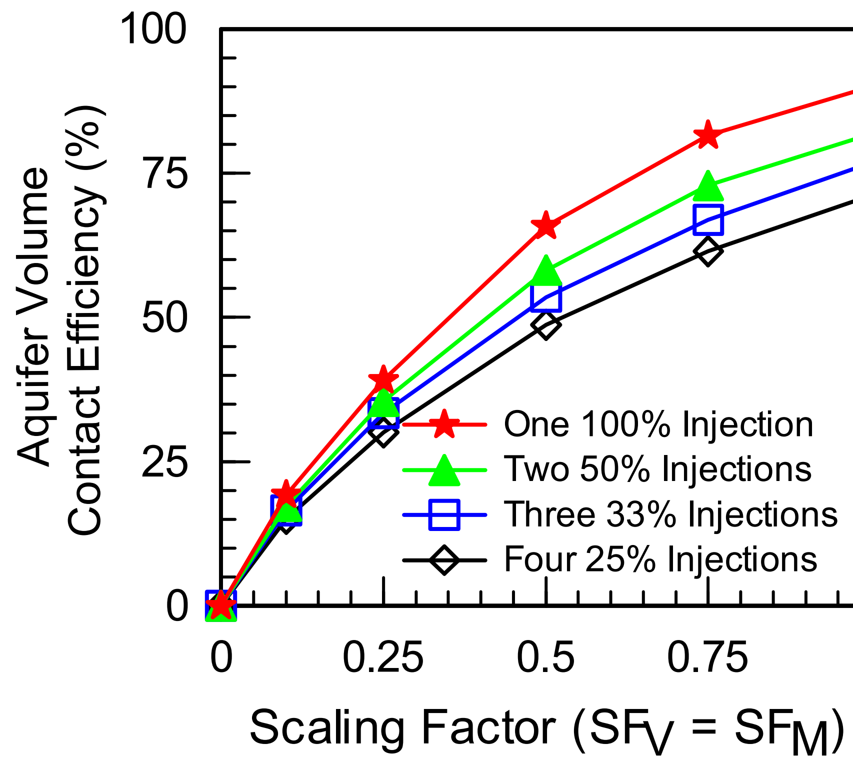


- Effect Water Injection Volume
  - Increasing SF_M (more MnO_4) increases contact efficiency
  - For $SF_M > 0.5$, large injection volumes have less benefit



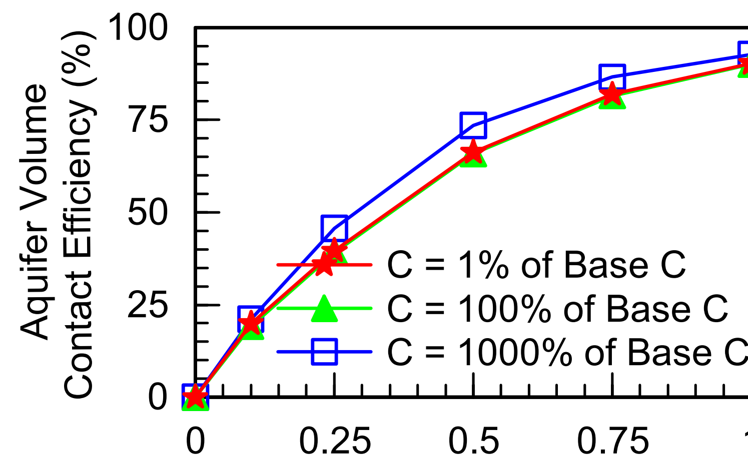
RT3D Sensitivity Analysis

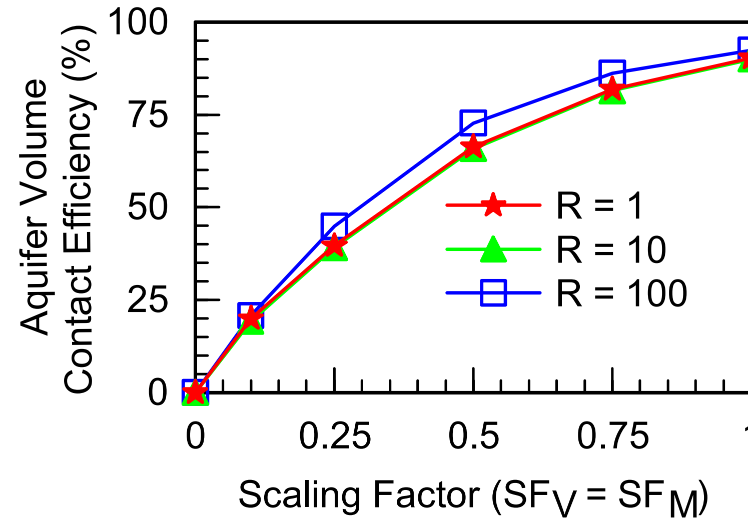
- Evaluate Impact of Multiple Injections
  - Total volume constant
  - Total MnO_4 constant
- Results
  - One large injection slightly more effective than four small injections
  - Four small injections much more effective than one small injection
  - Multiple injections has lower risk of downgradient migration



RT3D Sensitivity Analysis

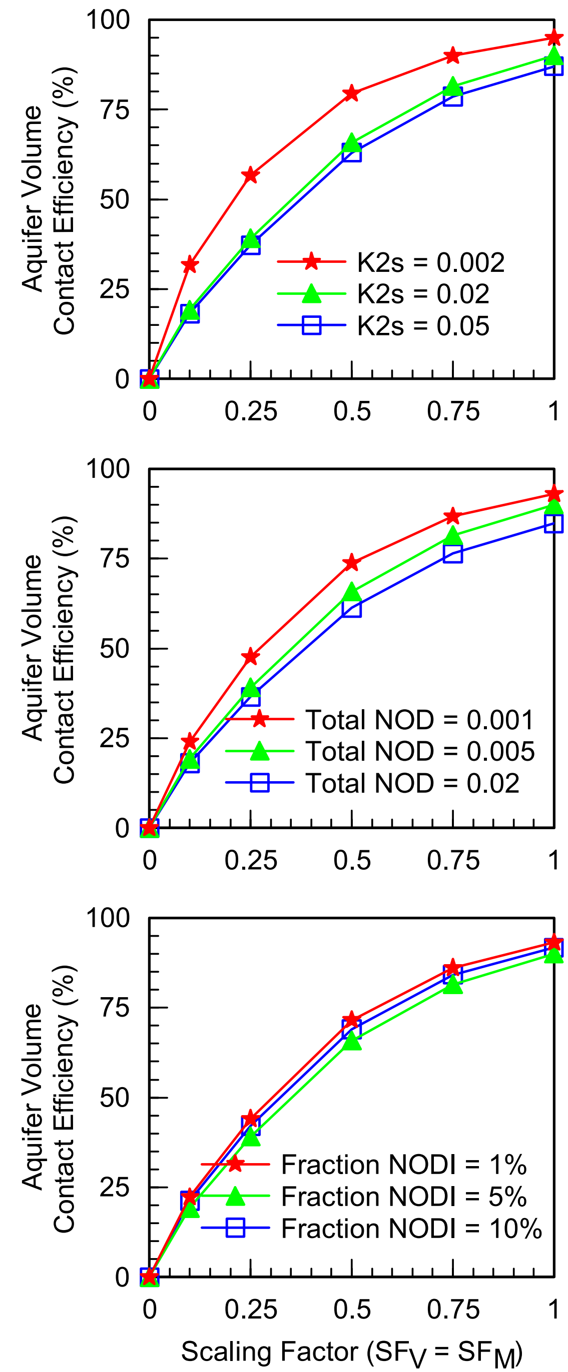
- Initial Contaminant Concentration
  - Minimal effect on E_V
  - Assumes you provide enough MnO_4
  - No NAPL in model
- Contaminant Retardation Factor
  - Minimal effect on E_V
  - Assumes you provide enough MnO_4





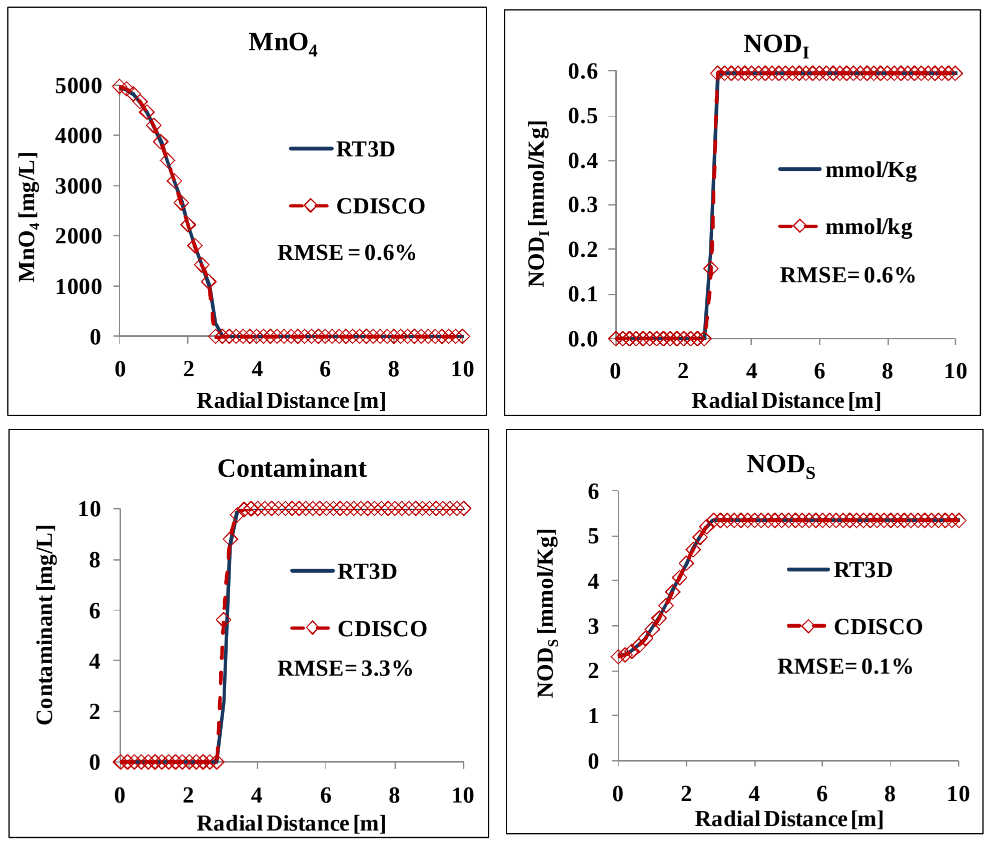
RT3D Sensitivity Analysis

- NOD Kinetics
  - Slow NOD rate
  - Total NOD
  - Fraction NOD_I
- Results
  - Contact efficiency sensitive to both Total NOD and NOD kinetics
  - Cannot use simple design curves to estimate contact efficiency
  - Need ‘simple’ spreadsheet model for design



Spreadsheet Design Tool

- CDISCO – Conceptual Design of ISCO
  - MS Excel based Numerical Model
  - Developed jointly with ER-0623
- Mechanics
  - MnO_4 transport and consumption
  - Based on series of CSTRs
  - NOD kinetics identical to RT3D
  - Includes cost estimating tool to aid in comparing alternatives
- Model Validation
  - Results 'identical' to full RT3D for homogeneous aquifers

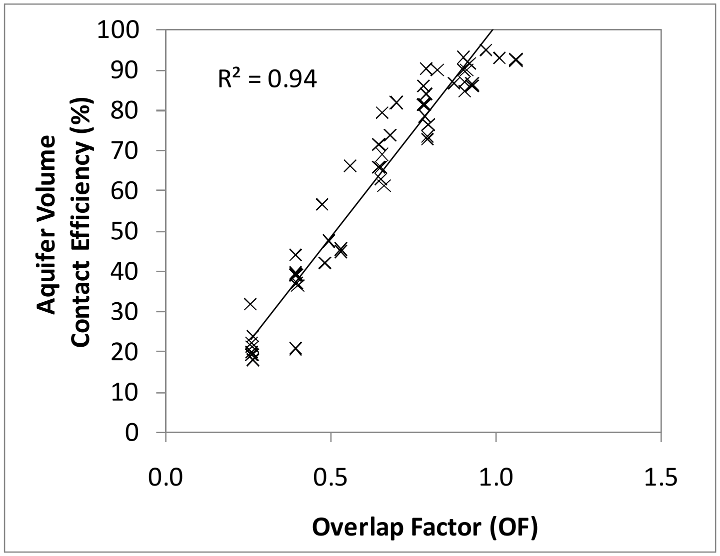


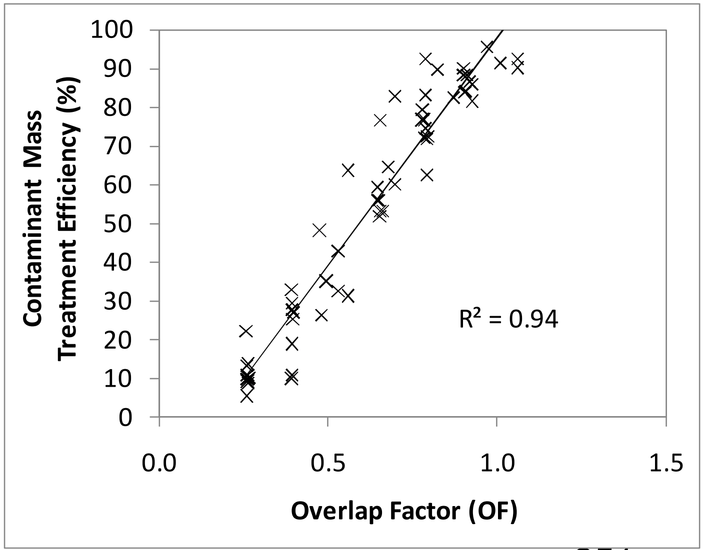
How to Design an Injection System

1. Enable Macros
2. Enter site data
3. Enter Design Criteria
   a. Target MnO_4 concentration (typical ~ 100 – 1000 mg/L)
   b. Target contact time (typical ~ 10 – 100 days)
   c. Overlap Factor (OF)
4. Click 'calculate' (run MnO_4 transport model)
5. Enter cost data
6. Review cost summary
7. Revise design and repeat model run

Overlap Factor (OF)

- Overlap Factor (OF)
  - Well Spacing = 2*ROI / OF
  - ROI = radius of influence
- CDISCO calculates ROI
  - Minimum MnO_4 concentration after __ days
- User must pick OF
  - Currently, no guidance on correct OF
  - Increasing OF increases cost
- Comparison of RT3D and CDISCO
  - Obtain E_V and E_M from 3D heterogeneous simulations
  - Obtain ROI from CDISCO
- Conclusion
  - OF between 1.0 and 1.5 generates good results





Site Data

1. Model run parameters
   a. simulation duration
   b. time step
2. Hydrogeologic characteristics
   a. Permeability
   b. Porosity
   c. effective thickness
3. NOD parameters
   a. Total NOD
   b. Fraction instantaneous
   c. Slow NOD rate coefficient
4. Oxidant and contaminant info
5. Injection info
   a. Injection well diameter and design flow per well
   b. Hours per day of injection and days of injection
6. Design criteria
   a. Target oxidant concentration and contact time
   b. Radius of influence overlap factor (OF)

Hydrogeologic Characteristics		
Top of Injection Interval	30	ft bgs
Bottom of Injection Interval	40.00	ft bgs
Aquifer Thickness	10	ft
Thickness of Mobile Zone (Z)	10.0000	ft
Porosity	0.20	L/L
Longitudinal Dispersivity	2.0000	ft
Hydraulic Conductivity (k)	50.00	ft/day
Depth to Water Table	15	ft
Soil and NOD Characteristics		
Bulk Density	1.60	Kg/L
NOD	1	g/Kg
Fraction Instantaneous	0.20	
Second Order Slow NOD Consumption Rate (Ks)	0.1000	L / mmol - d
Oxidants Information		
Name of Oxidant	Permanganate (MnO_4^-)	
Molecular Weight of Oxidant	118.94	g/mol
Initial Oxidant Concentration	0.00	mg/L

Cost Data

1. Categories
   a. Prime contractor (mobe, hourly labor, expenses)
   b. Subcontractor (mobe, hourly labor, expenses)
   c. Reagent, materials and equipment rental
2. Activities
   a. Fixed costs (design, permitting, etc.)
   b. Injection well or probe installation
   c. Reagent injection

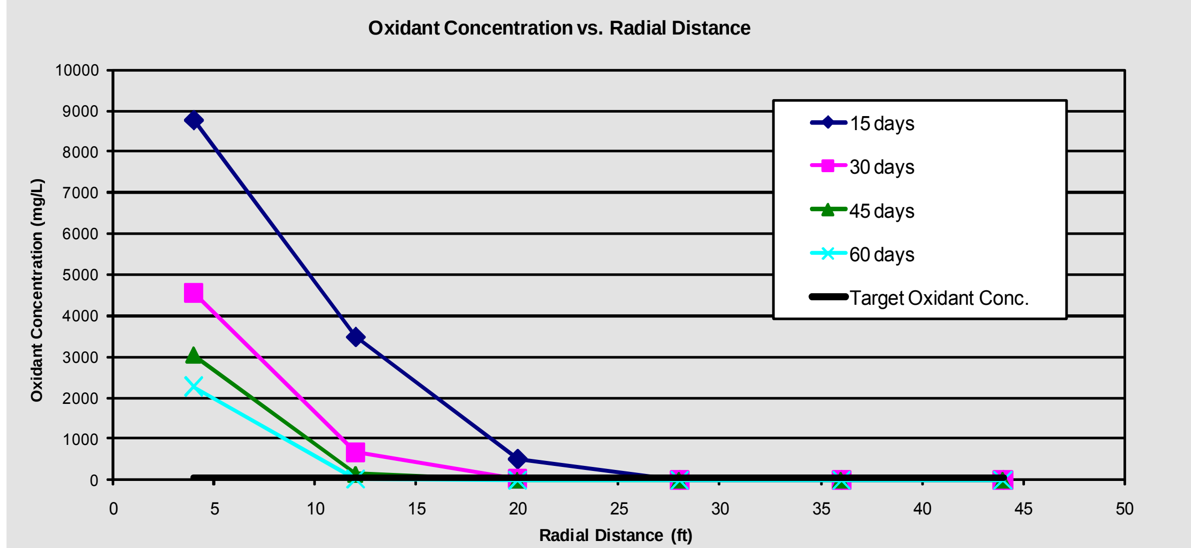
Installation and Injection Costs for:
Injection through Direct Push Probes

Information on the labor and materials required for ISCO injection by direct push injection (DPI) is entered on this page. Drilling and injection is assumed to be performed by a subcontract driller with supervision by the prime contractor. In this approach the oxidant is injected in a single operation where the DPI equipment drives the rod to the desired depth immediately followed by oxidant injection over an aquifer thickness equal to the injection screen length. The rod is moved to a different depth and the operation is repeated. Once injection is complete over the entire injection interval, the rod is removed, the boring grouted and the DPI equipment is shifted to a new location. DPI injections can be performed into a single probe or into multiple probes simultaneously.

1	***Injection Information***		
a	Top of Injection Interval	30	ft
b	Bottom of Injection Interval	50	ft
c	Injection rate to be used in Design	3,000	gpd/probe
d	Number of probes injected simultaneously, or number of probes drilled and injected per day	5	
2	***Fixed Costs***		
a	Prime contractor mobilization	500	$
b	Subcontractor mobilization	2,000	$
c	Water Supply	500	$
d	Piping and other equipment for oxidant preparation and injection	2000	$
e	Time required for equipment setup and removal	8	person - hr
f	Average labor rate for equipment setup and removal	100	$/hr
g	Labor cost for setup and removal	800	$
h	**Total fixed cost**	**5,800**	**$**
		0	
3	***Prime Contractor Information and Daily Costs***		
a	Prime contractor personnel on-site each day of injection	1	person(s)
b	Average labor rate of prime contractor personnel	100	$/hr
c	Hours billed per person per day	10	hr/person/day
d	Per Diem (e.g., meals, travel, vehicle rental, lodging)	200	$/person/day
e	Additional costs (consumables, H&S, and monitoring equipment)	200	$/day
f	Injection equipment rental costs (pumps, tanks, hoses, etc.)	200	$/day
g			
h	**Total daily cost for prime contractor**	**1,600**	
		4,800	
4	***Subcontractor Information and Daily Injection Costs***		
a	Drilling Equipment to be used		
b	Daily cost for DPT equipment and operator	3000	$/day
f	Additional material and IDW daily costs	200	$/day
g	**Total daily cost for subcontractor**	**3,200**	**$/day**
5	***Daily Costs for Injection using DPT Equipment***		
a	**Injection costs per day**	**4,800**	**$/day**

Permanganate Design Tool

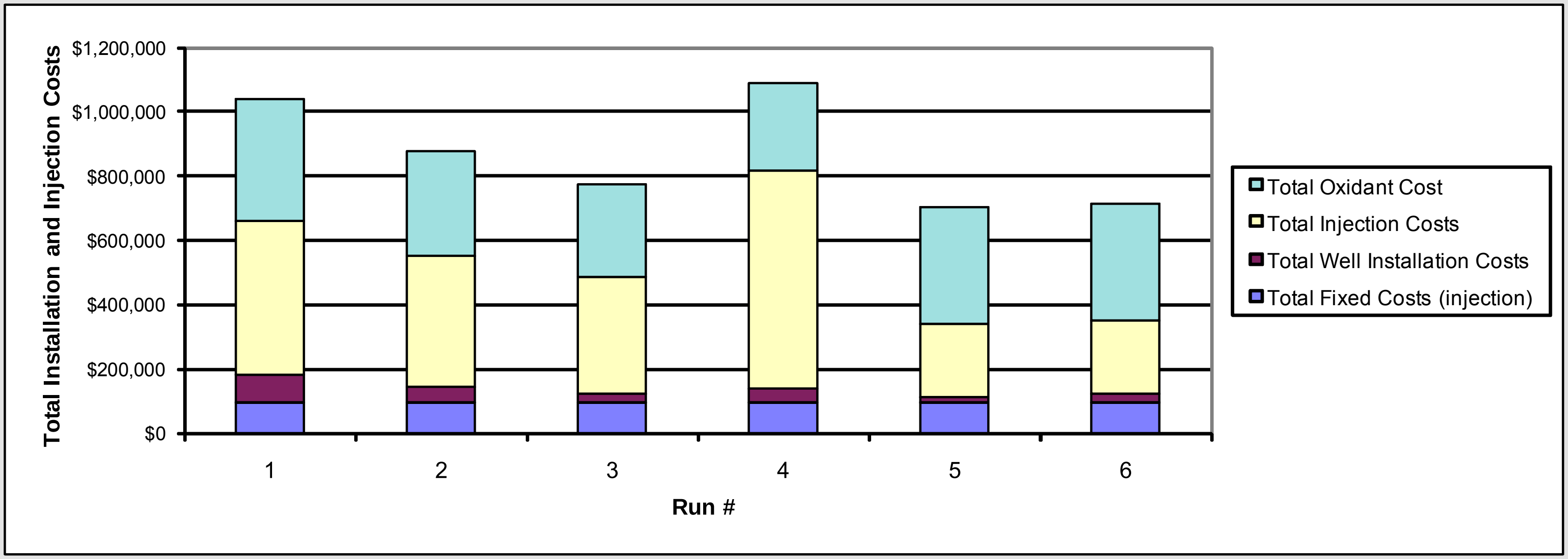
- Typical CDISCO Results
  - Generates graphs of MnO_4 conc. vs distance for different injection conditions
- Determines effective Radius of Influence (ROI) based on
  - Minimum MnO_4 Conc.
  - Contact Time
- Determines injection well spacing based on
  - ROI
  - Overlap factor



Selected	Run Number	Injection Duration	Aquifer Thickness	Thickness of Mobile Zone	NOD Fraction Instantaneous	NOD (g/kg)	Slow NOD Rate	Injection Oxidant Conc (mg/L)	Injection Rate gal/Day	ROI	Minimum Oxidant Conc to Calc ROI	Target Number of Days to Calc ROI
✓	1	3	20	10	0.1	5	0.001	10,000	3,000	10.41	50	30
✓	2	5	20	10	0.1	5	0.001	10,000	3,000	14.46	50	30
✓	3	10	20	10	0.1	5	0.001	10,000	3,000	21.25	50	30
✓	4	10	20	10	0.1	5	0.001	5,000	3,000	15.56	50	30
✓	5	10	20	10	0.1	5	0.001	20,000	3,000	27.23	50	30
✓	6	5	20	10	0.1	5	0.001	20,000	3,000	19.64	50	30

Design Tool Summary

Run	1	2	3	4	5	6
Total Fixed Costs (injection)	$94,800	$94,800	$94,800	$94,800	$94,800	$94,800
Total Well Installation Costs	$85,667	$47,700	$25,367	$41,000	$18,667	$29,833
Total Injection Costs	$478,800	$410,400	$364,800	$684,000	$228,000	$228,000
Total Oxidant Cost	$378,547	$324,469	$288,417	$270,391	$360,521	$360,521
Total Installation and Injection Costs	$1,037,814	$877,369	$773,384	$1,090,191	$701,988	$713,155
Number of probes or wells required	35	18	8	15	5	10
NOD (g/kg)	5	5	5	5	5	5
Injection Oxidant Concentration	10000	10000	10000	5000	20000	20000
Injection Oxidant Mass (lbs)	26288	22533	20029	18777	25036	25036
Injection Duration (days)	3	5	10	10	10	5
Volume Injected per Day (gal/d)	3000	3000	3000	3000	3000	3000
Thickness of Mobile/Target Thickness	0.5	0.5	0.5	0.5	0.5	0.5



Additional Resources

- Software Download
  - http://docs.serdp-estcp.org/ (search for Design Tool)
  - http://www4.ncsu.edu/~rcborden/Design_Tool.html
- Technical Report
  - Design Tool for Planning Permanganate Injection Systems
- Websites
  - SERDP/ESTCP (http://docs.serdp-estcp.org)
    - In Situ Chemical Oxidation Initiative
    - Decision Support Tools for In Situ Chemical Oxidation
  - ITRC (http://www.itrcweb.org/gd_ISCO.asp)
    Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2nd Ed.
  - USEPA,
    In-Situ Chemical Oxidation - Engineering Issue
    http://www.epa.gov/ada/download/issue/600R06072.pdf

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:50 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo

Improved Field Evaluation of NAPL Dissolution and Source Longevity

Dr. Michael Kavanaugh
Malcolm Pirnie, Inc.

Dr. Mark Widdowson
Virginia Tech

Dr. Rula Deeb
Malcolm Pirnie, Inc.

Dr. Lloyd "Bo" Stewart
Praxis Environmental Technologies, Inc.

Project Team: ER-0833

- Malcolm Pirnie, Inc.
  - Michael Kavanaugh, Ph.D., P.E. (PI)
  - Rula Deeb, Ph.D. (Project manager)
  - Jennifer Nyman, Ph.D. (Deputy project manager)
- Praxis Environmental Technologies, Inc.
  - Lloyd "Bo" Stewart, Ph.D., P.E. (co-PI)
- Virginia Polytechnic Institute and State University
  - Mark Widdowson, Ph.D. (co-PI)
- GeoTrans, Inc.
  - Jim Mercer, Ph.D.

Acknowledgements

- Air Force (funding of the TEE pilot study)
  - Mr. Bill Lopp, AFCEE
- BEM (contractor at the site)

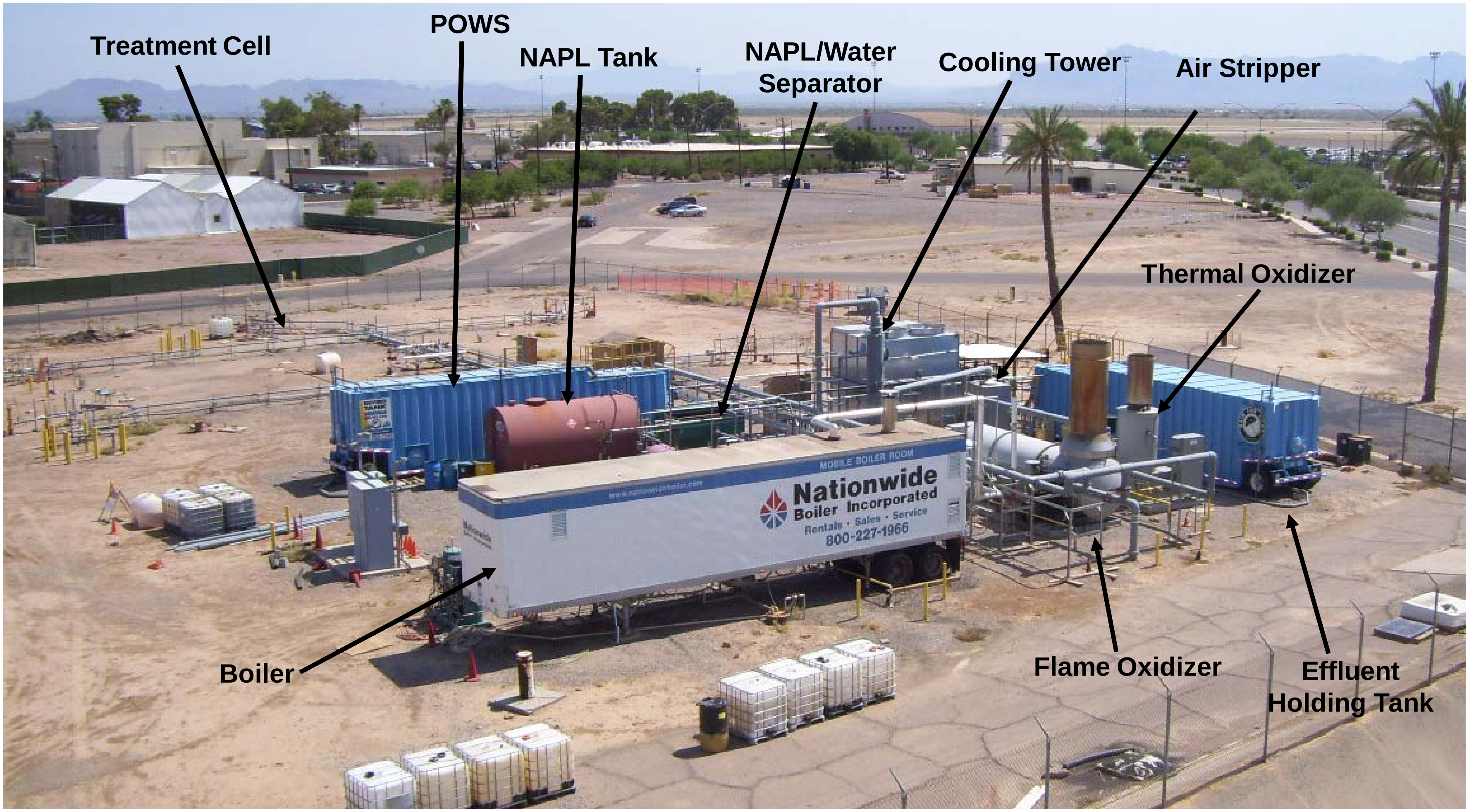
Decision-Making Tool for NAPL Source Zones

- Key challenge: Determining magnitude of NAPL source depletion needed to meet site Remedial Action Objectives (RAOs) at defined point of compliance.
- Technical challenges
  - Rate of LNAPL dissolution as function of time
  - Accurate prediction of transformation processes for chemicals of concern (e.g., benzene, naphthalene)
- Proposed approach
  - Field determination of pre and post remediation rates of dissolution based on field estimates of mass transfer coefficients
  - Application of SEAM3D fate and transport model combined with flow model to assess the potential effectiveness of source removal scenarios

Demonstration Site

- Site ST012, former Williams AFB, AZ
- Multi-component NAPL source zone
  - JP-4 fuel, BTEX, naphthalene
- Variety of NAPL architectures
  - Extensive smear zone from rising water table; dispersed ganglia
  - Pooled NAPL below low permeability, semi-confining units
- Pilot test of Thermal Enhanced Extraction (TEE) by USAF
  - Duration: October 2008 – May 2009
  - Mass transfer tests before and after TEE
  - Data interpretation and simulation of various source depletion options using SEAM3D

Demonstration Site



View facing northeast across Site ST012 (July 2, 2008)

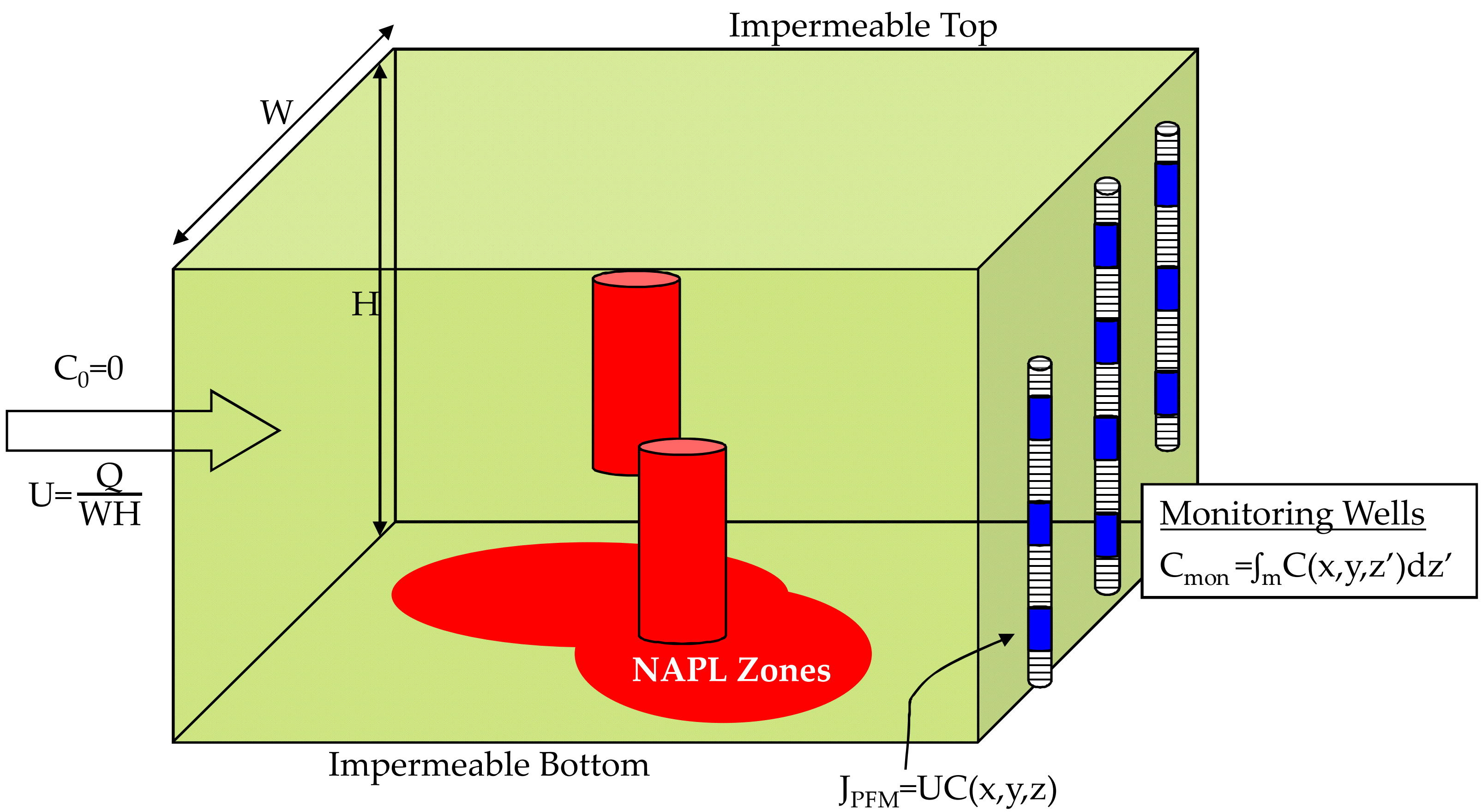
Multi-Scale Measures of Mass Dissolution Rate

- Sweep the NAPL source zone with clean water
- Collect multi-scale data for water movement through the source zone
- Collect multi-scale data for concentrations and mass flux of target chemicals

Field Technologies

- Conventional Monitoring Well Data
  - Concentration
  - Water level
  - NAPL thickness and recharge rate
- Integrated Pumping Test (IPT)
  - Modified to include water injection
  - Modified to include tracer test (e.g., bromide)
  - No new capital if Pump &Treat system is in place
- Passive Flux Meters (PFMs)
  - Vertically segmented within multiple monitoring wells

Conventional Data with PFMs Collected Downgradient



Nomenclature

W = width of flow cross-section through NAPL zone

H = height of flow cross-section through NAPL zone

Q = volumetric flow rate through cross-section

U = velocity of groundwater

C_0 = ambient concentration entering NAPL zone

C(x,y,z) = concentration at position x,y,z

C_{ext} = concentration in extracted groundwater

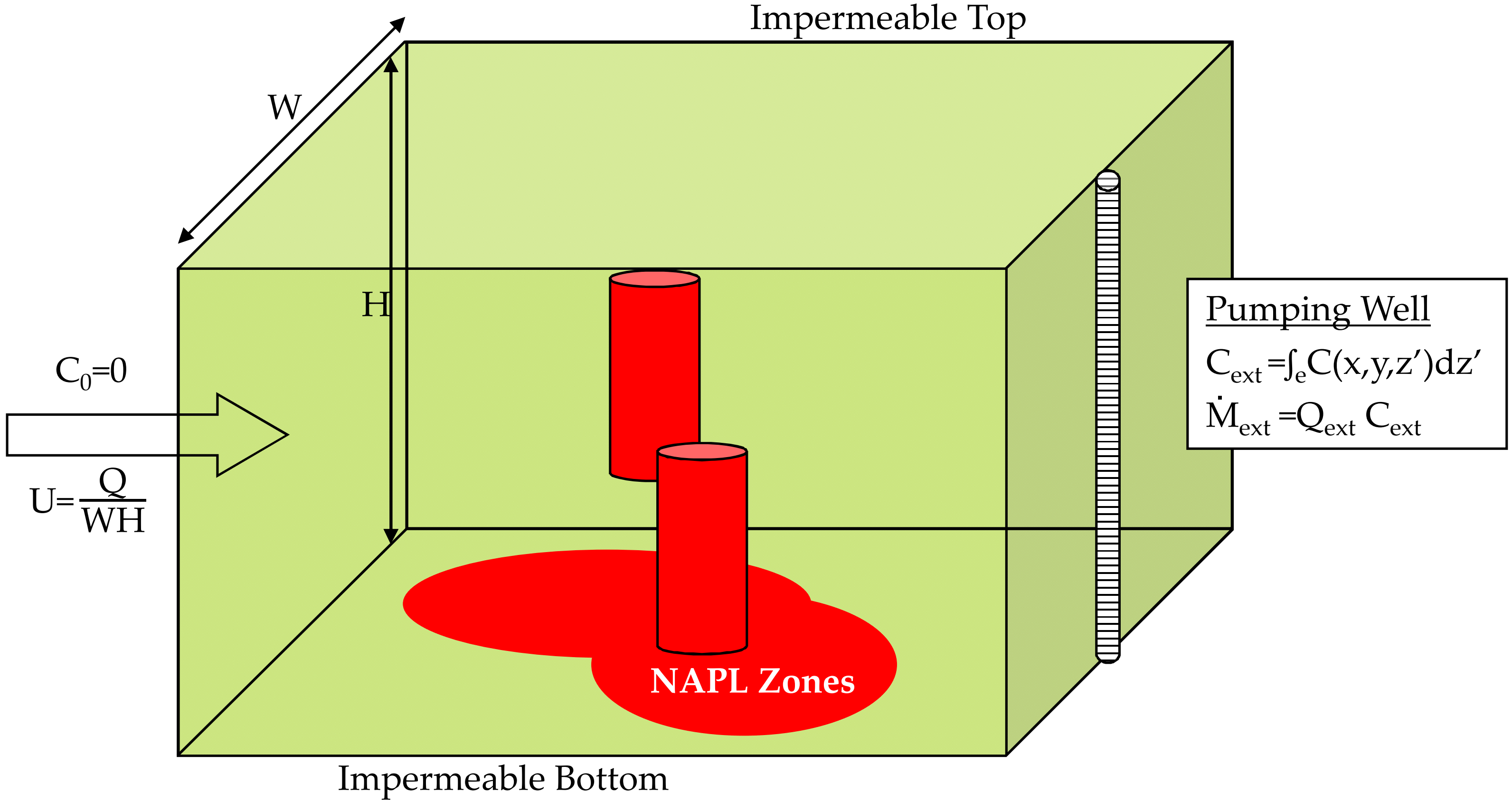
Q_{ext} = volumetric extraction rate

M_{ext} = mass extraction rate of contaminant

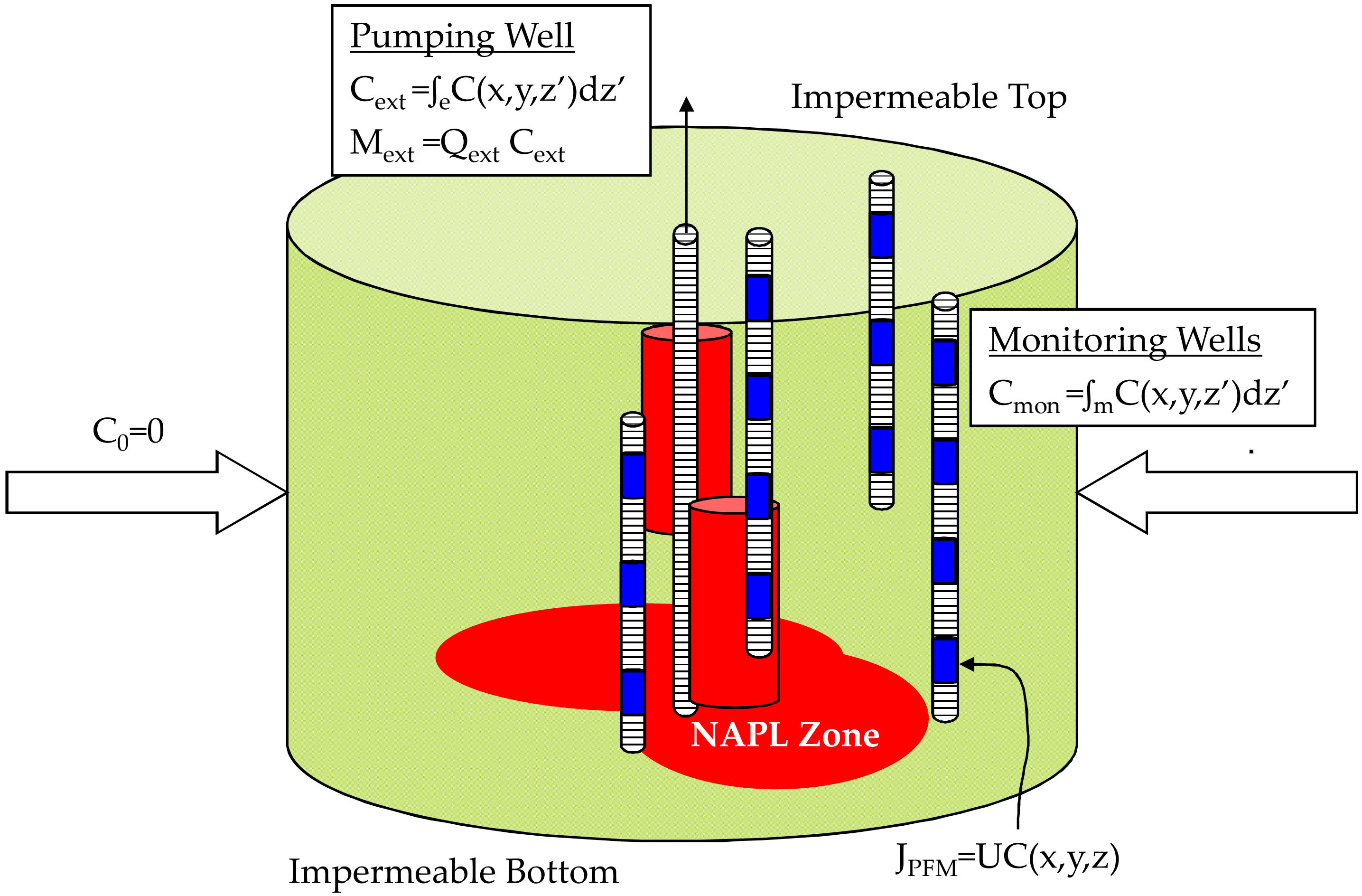
C_{mon} = concentration in monitoring well

J_{PFM} = contaminant flux measured by PFM at x,y,z

Mass Dissolution from IPT Collected Downgradient



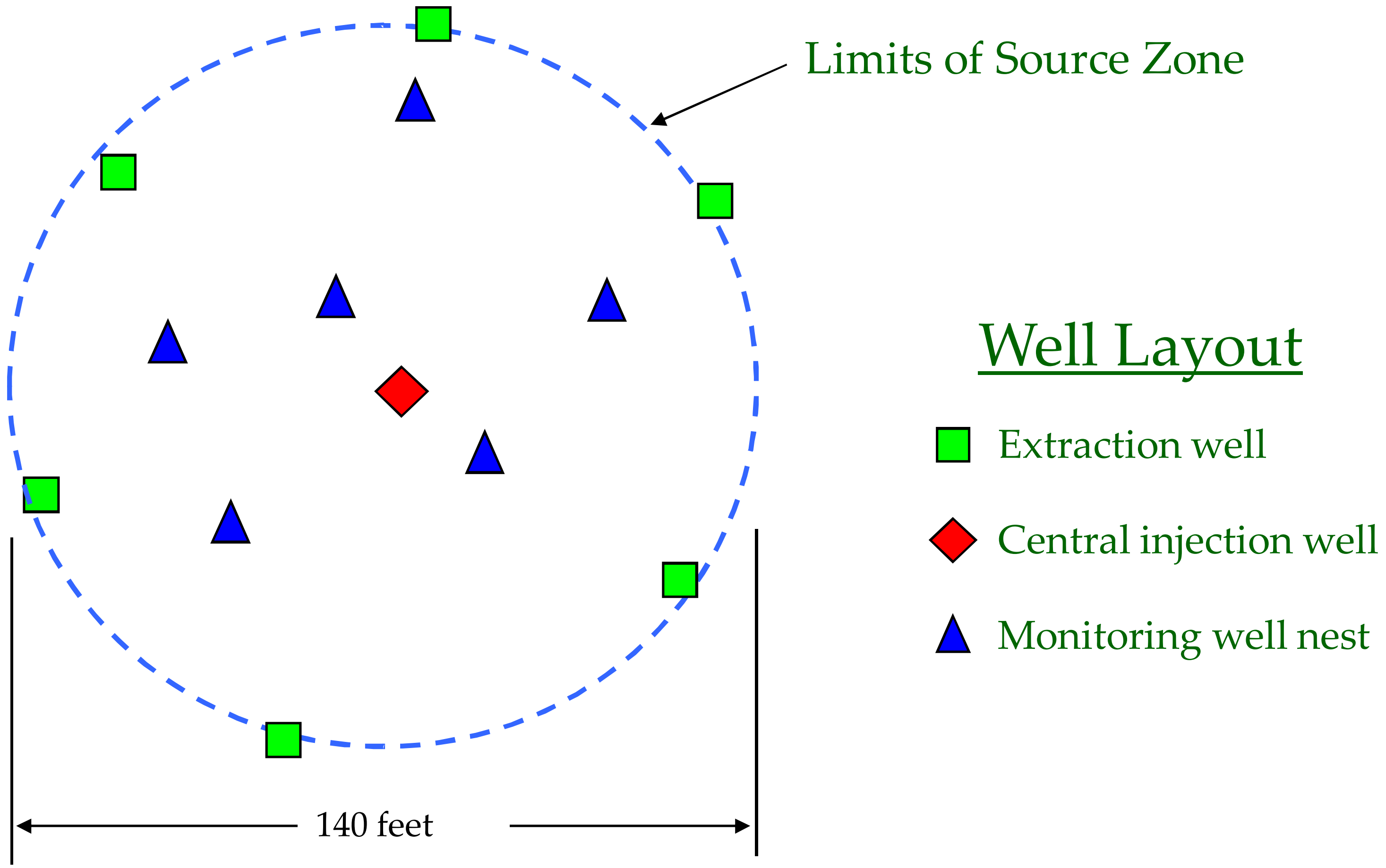
Multi-Scale Mass Dissolution Measurements in Source Zone



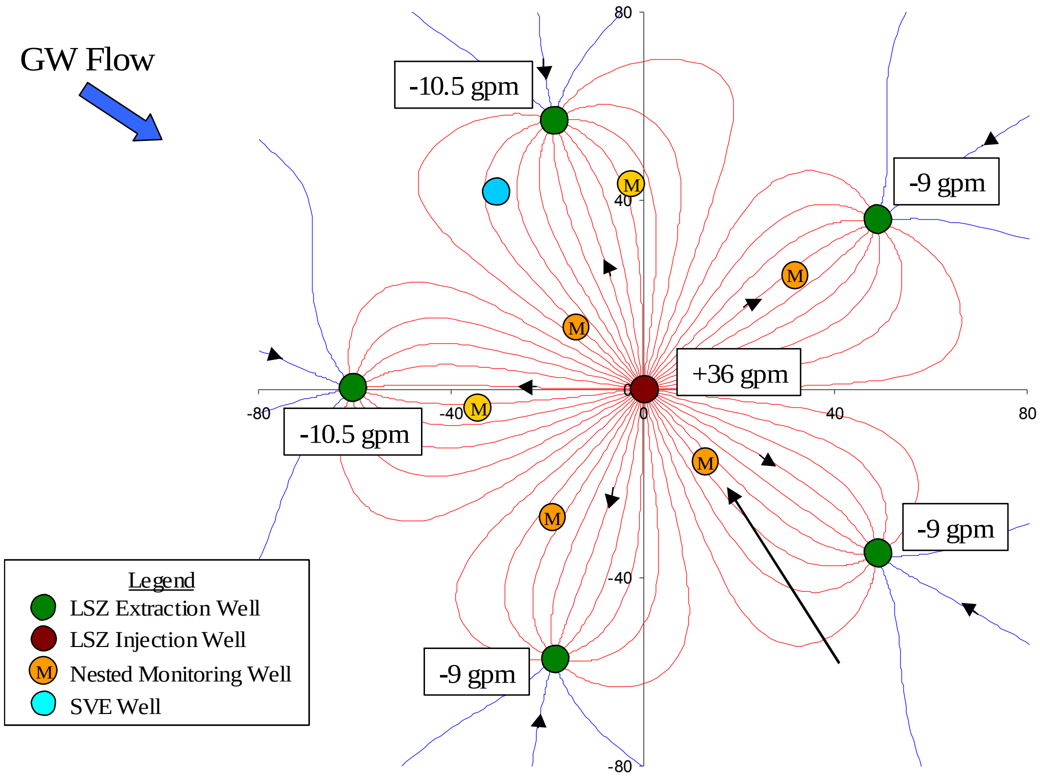
Integrated Pumping Test

- Water Injection to Sweep Source Zone
- Tracer Test to Define Flow Intervals
  - Bromide
  - Multi-Level Sensors
- Defines Mass Dissolution on a Large Scale
  - Imposed flow rate higher than ambient groundwater flow
  - Yields a maximum mass dissolution rate
  - Mass dissolution on the scale of the DNAPL source dimensions

Plan View of Wells

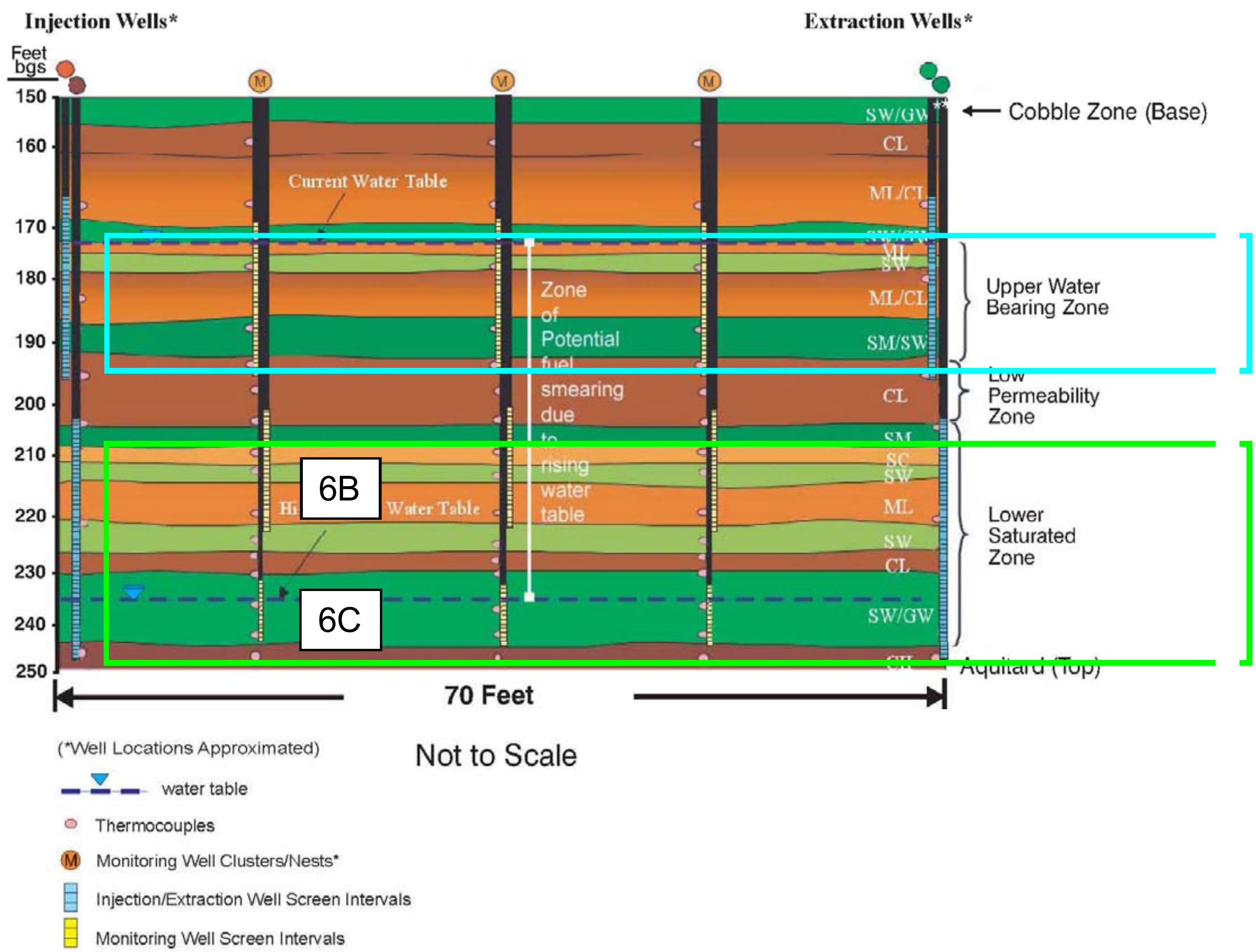


Idealized Streamlines during IPT

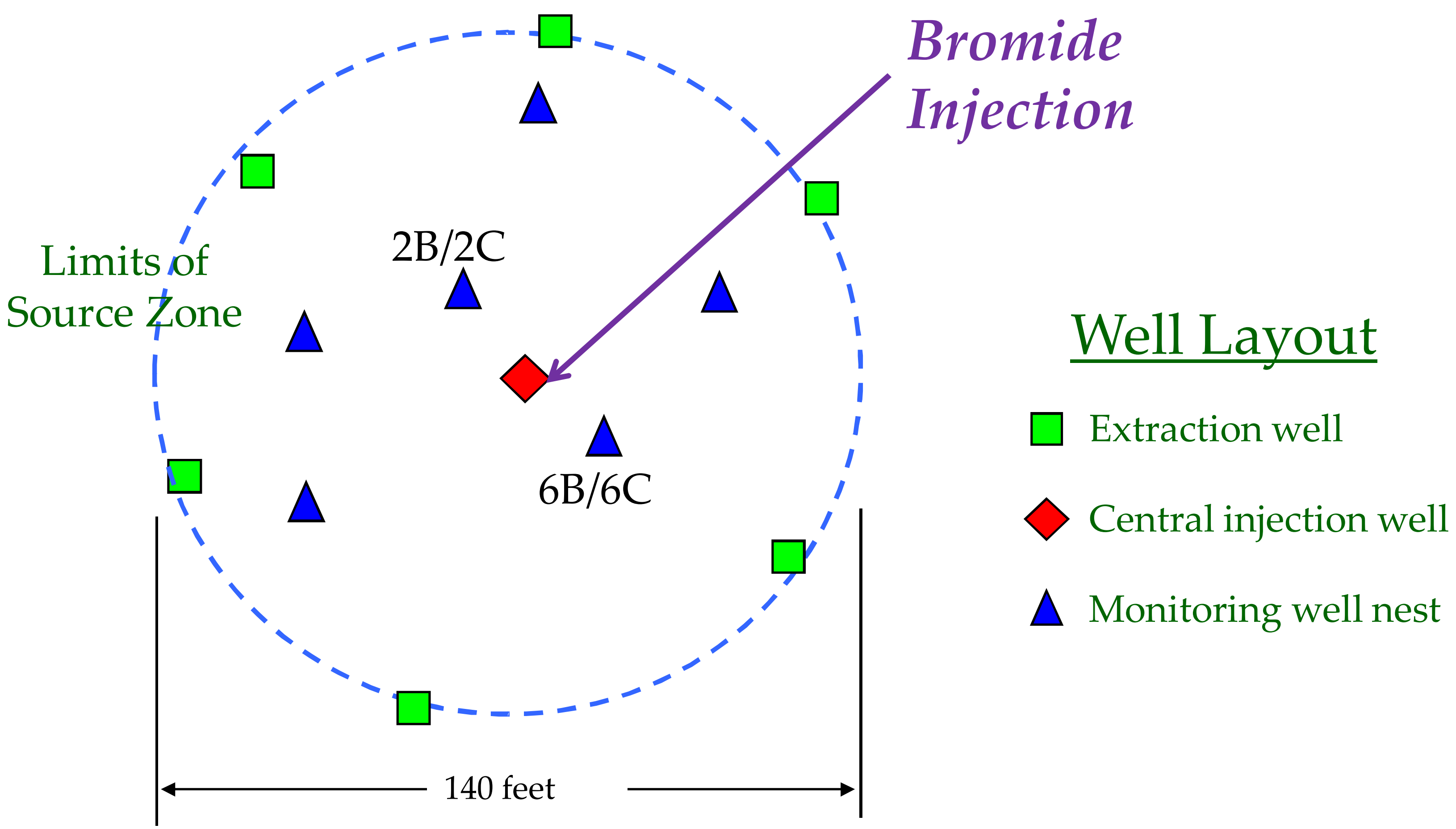


Streamlines Depicting Idealized Groundwater Flow During Mass Transfer Test

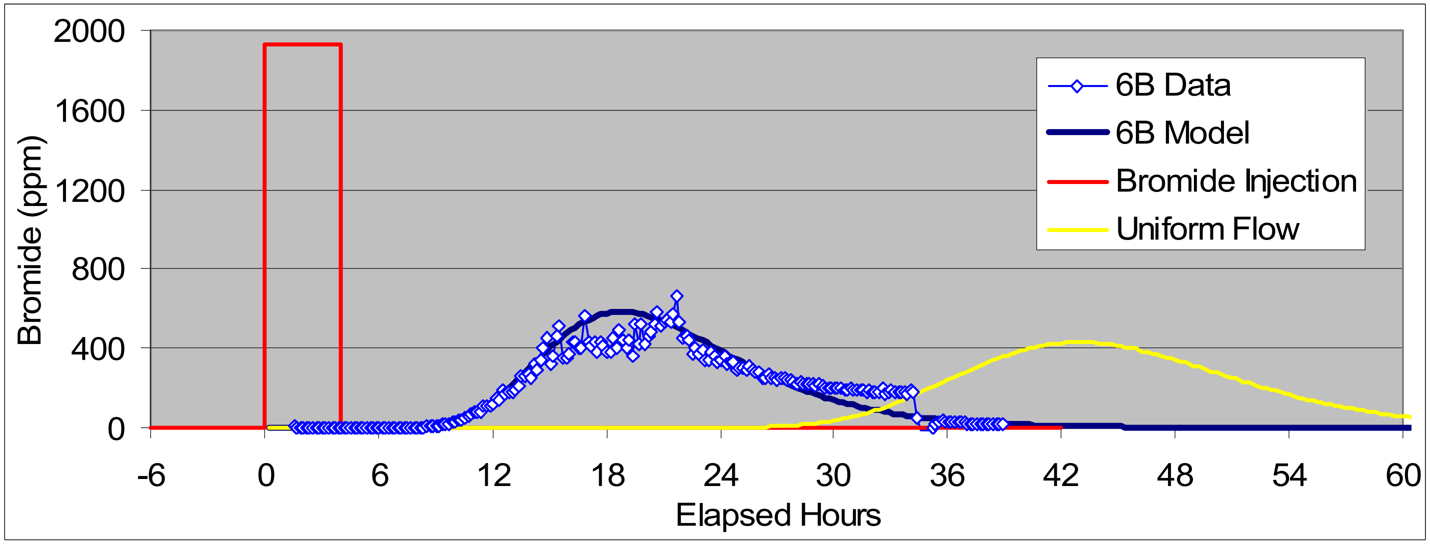
Conceptual Cross-Section

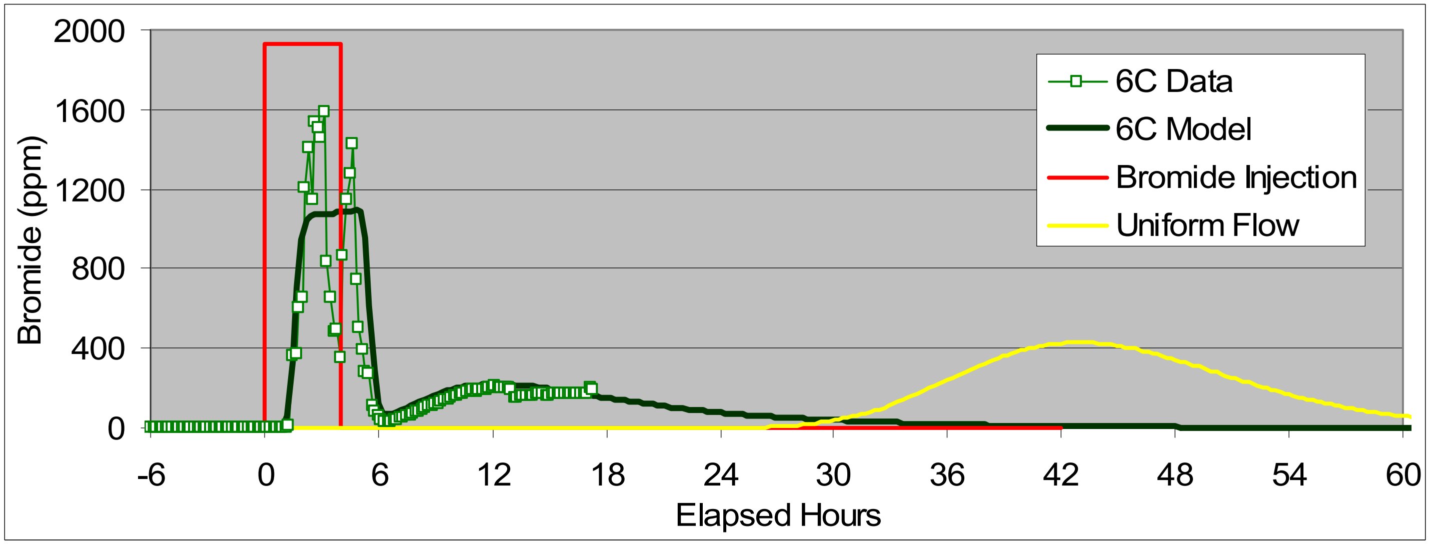


Tracer Test Layout

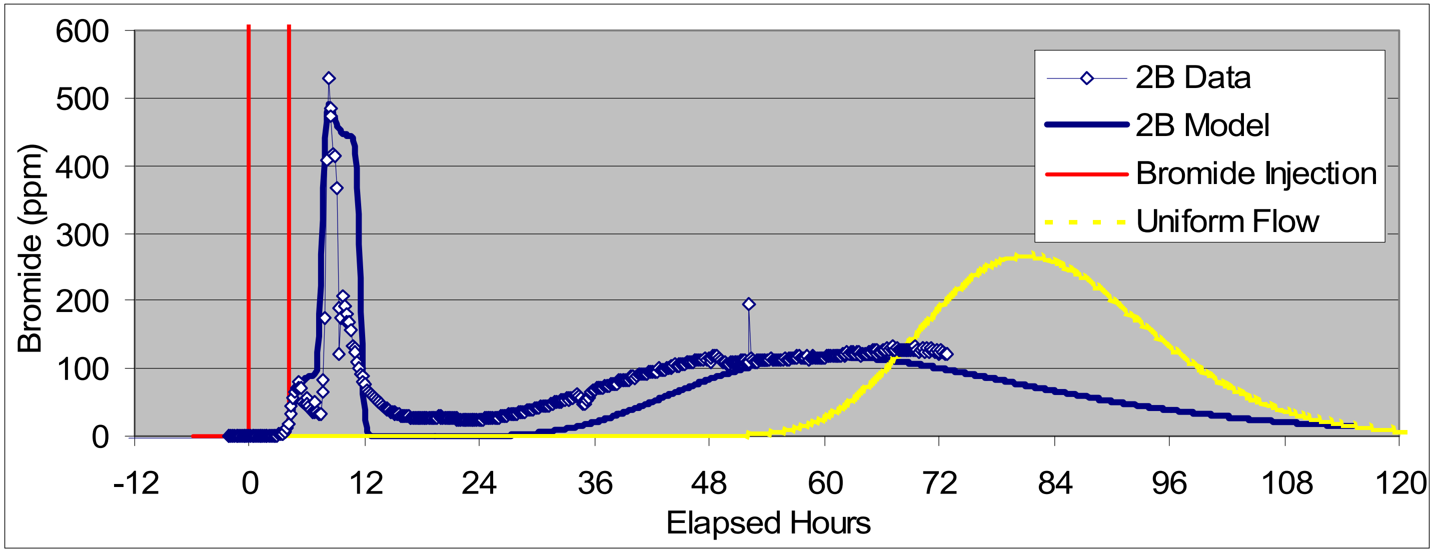


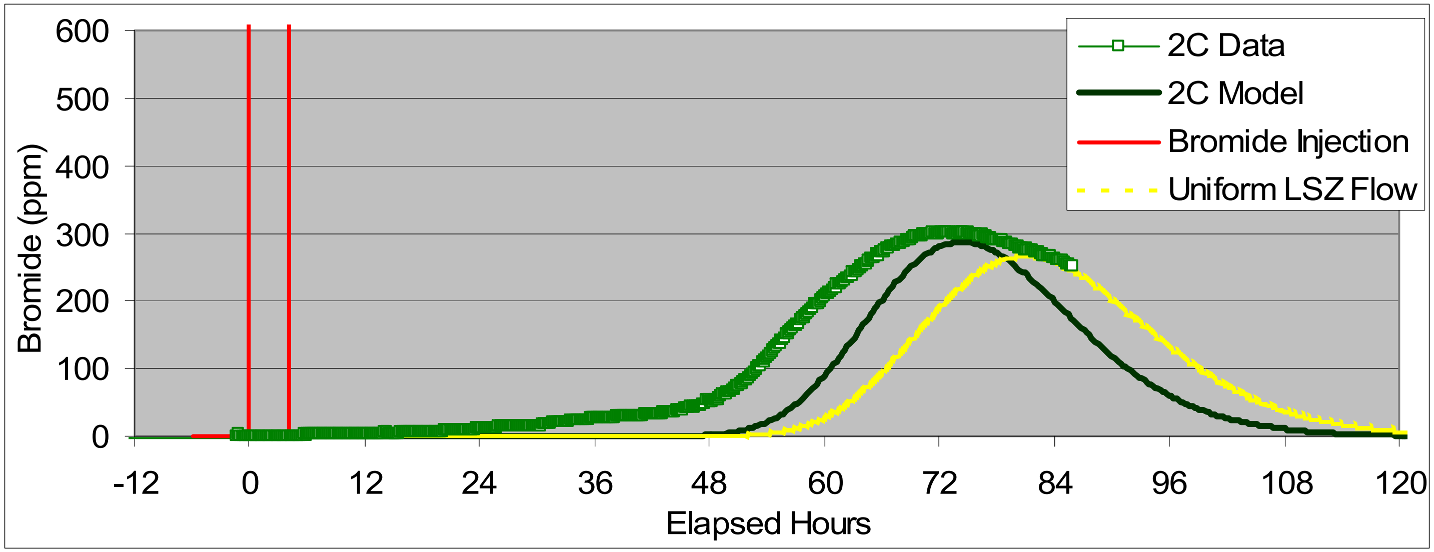
Bromide Tracer Responses





Bromide Tracer Responses

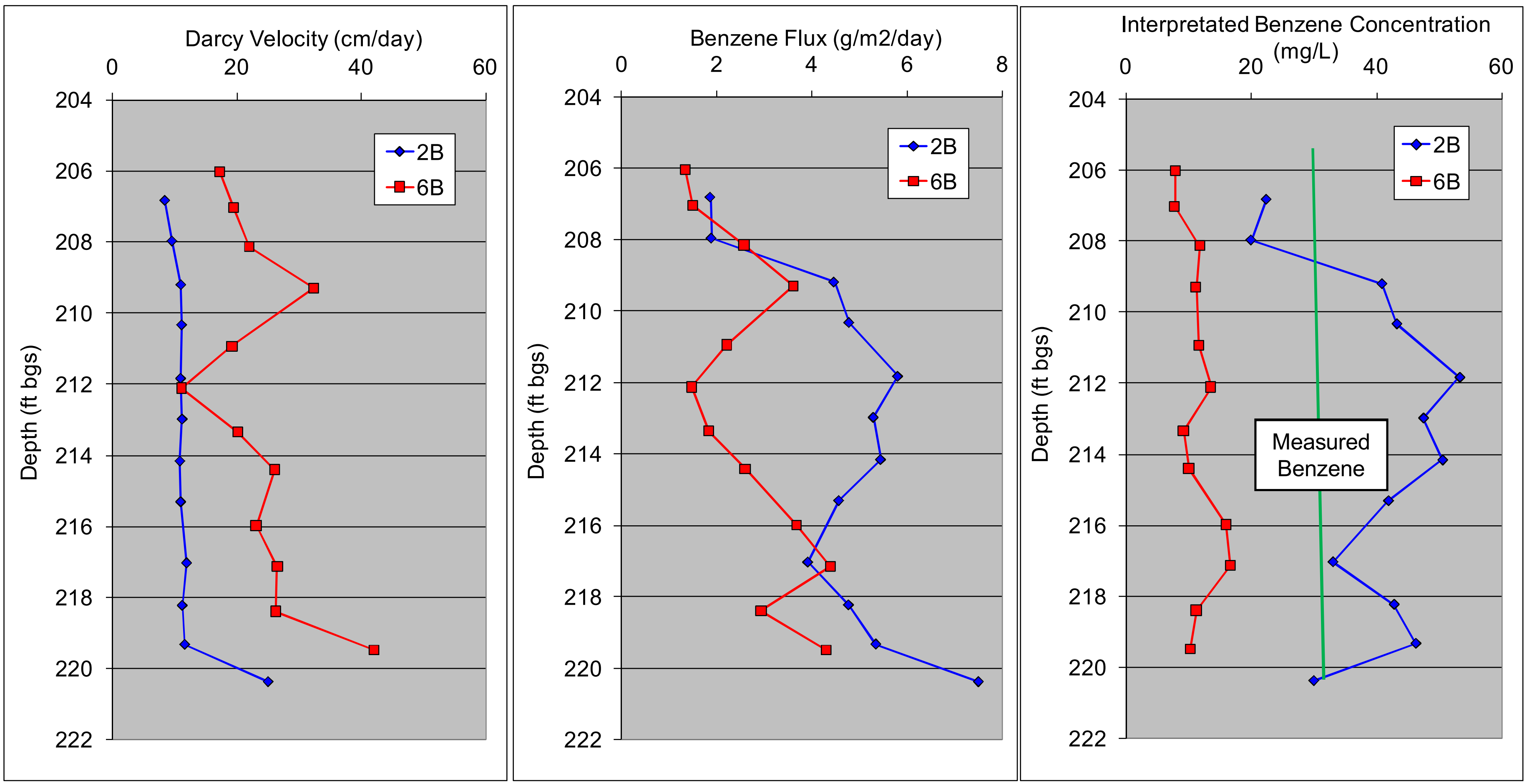




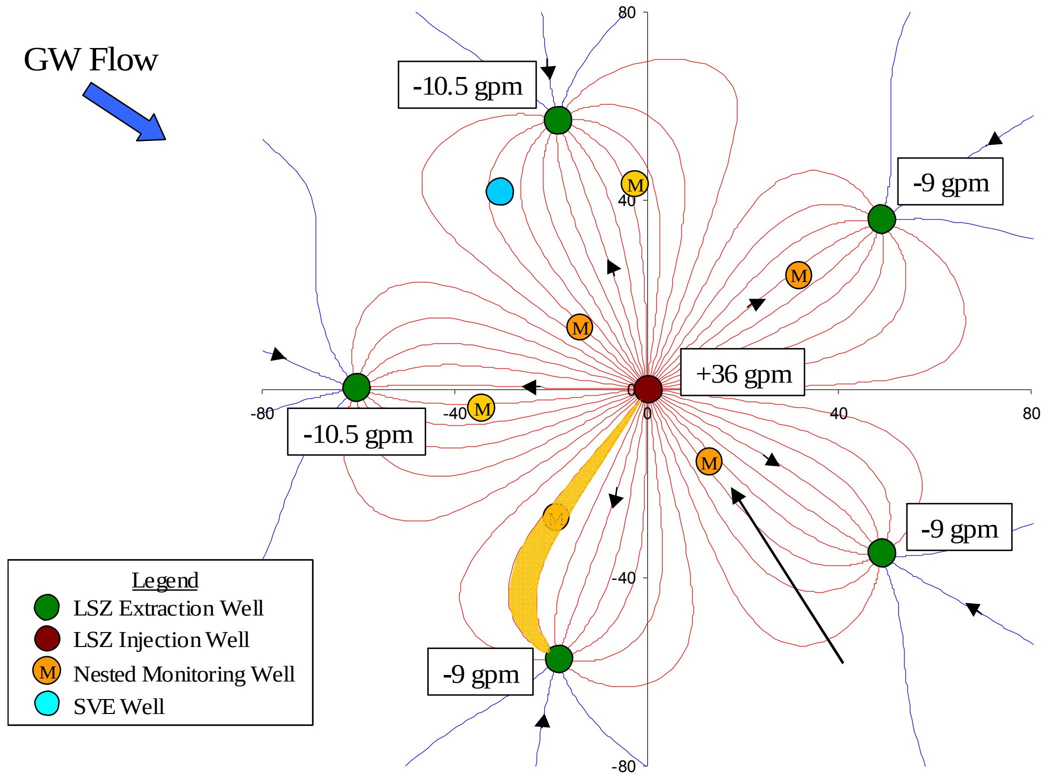
Passive Flux Meters (PFMs)

- PFMs are segmented nylon mesh tubes filled with a sorbent/tracer mixture
- Inserted into monitoring wells to passively intercept groundwater flow
- Permeable sorbent (e.g., GAC) retains dissolved contaminants
- Preloaded alcohol tracers are leached as groundwater flows through the PFM
- PFM provides vertical profiles of horizontal water and contaminant fluxes

Passive Flux Meters



Idealized Streamlines during IPT



Streamlines Depicting Idealized Groundwater Flow During Mass Transfer Test

Interpretation of IPT

- Large-scale bulk mass transfer coefficient determined from the IPT (yields a maximum value):

$$M^{NAPL}_{source,i} = K_{i,IPT} C_i^{eq} V_{IPT} = QC_{i,ext}$$

$$K_{i,IPT} = \frac{QC_{i,ext}}{C_i^{eq} V_{IPT}}$$

  - M^{NAPL} = total mass extraction/dissolution rate of component *i*
  - Q = total extraction rate
  - C_i^{eq} = equilibrium aqueous concentration
  - $C_{i,ext}$ = concentration of i in extracted groundwater
  - $K_{i,IPT}$ = bulk mass transfer coefficient
  - V_{IPT} = sweep volume

Interpretation of PFMs

- Streamtube-scale bulk mass transfer coefficient determined from the IPT and PFM:

$$K_{i,streamtube} = \frac{J_{i,PFM} A_{PFM}}{V_{streamtube} C_i^{eq}}$$

  - $J_{i,PFM}$ = contaminant flux measured by the PFM
  - A_{PFM} = streamtube cross-sectional area at the PFM
  - $V_{streamtube}$ = volume of soil flushed by clean water intersected by the PFM
  - C_i^{eq} = equilibrium aqueous concentration
  - $K_{i,streamtube}$ = streamtube-scale bulk mass transfer coefficient

HOW DO WE USE THE MULTI-SCALE MASS DISSOLUTION MEASUREMENTS?

Modeling

Modeling Objectives

- Validate results of MMT data interpretation
  - Source zone parameters
- Predict post-TEE conditions
  - New equilibrium plume size and concentrations
- Quantify time of remediation estimates for source longevity in support of decision making
  - Remedial action work plan
  - Evaluate range of uncertainty
  - Additional mass removal scenarios

Tools and Steps

Calibrated Site Model
- Groundwater flow (MODFLOW)
- Solute transport and attenuation (SEAM3D)
  - NAPL source zone

Validate Source Zone Model
- Data
  - Pre-TEE MTT
  - Post-TEE MTT
- SEAM3D NAPL Package
  - NAPL mass
  - Mass transfer rate

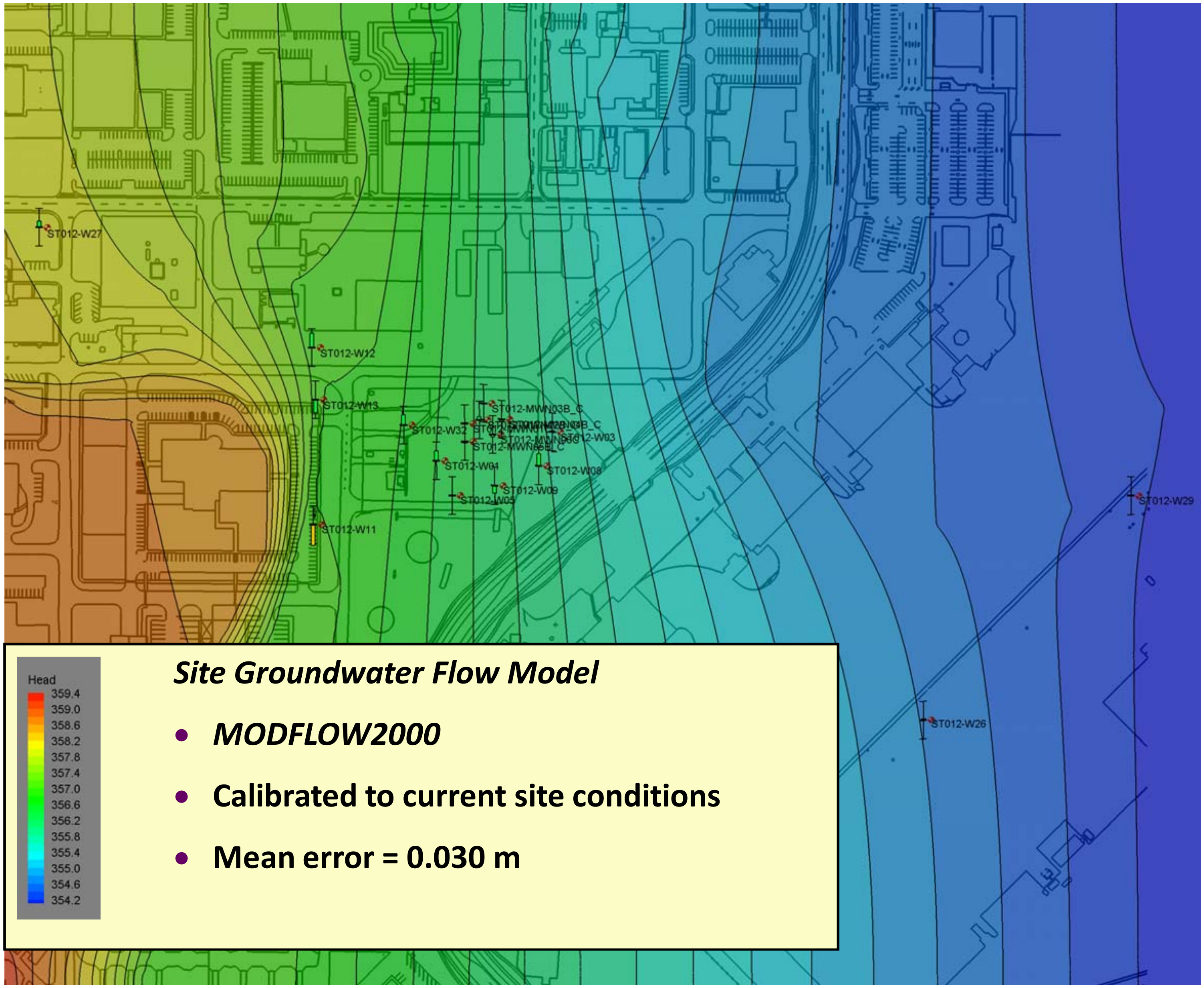
Decision-Making Tool
- Updated site model
- Plume and source longevity
  - Post-Tee conditions
  - Remediation timeframe

Calibrated Site Model

- Groundwater flow – MODFLOW 2000
- Solute transport and attenuation – SEAM3D
  - Physical transport
  - Biodegradation
    - Aerobic
    - Anaerobic
  - NAPL dissolution
    - Multi-component
    - Upscaled mass transport coefficient

MNA Modeling Objective

- Objective - Simulate current site conditions, including historical data
  - PHC transport coupled to NAPL dissolution and aerobic/anaerobic biodegradation
- Approach
  - Construct and calibrate groundwater flow model to match observed historical water level data
  - Calibrate a solute transport model to historic PHC concentrations and TEAP/redox conditions



Site Groundwater Flow Model

- ***MODFLOW2000***
- **Calibrated to current site conditions**
- **Mean error = 0.030 m**

Model Variables

- Hydrocarbon Compounds – NAPL
- Electron Acceptors (aq)
  - Oxygen
  - Nitrate
  - Sulfate
- Electron Acceptors (s)
  - Bioavailable Fe(III)
- End Products
  - Fe(II)
  - Sulfide
  - Methane

Solute Transport

Hydrocarbon Compounds: C_i

$$-\frac{\partial}{\partial x}\left(q_s C_i\right)+\frac{\partial}{\partial x}\left(\theta D\frac{\partial C_i}{\partial x}\right)+Q_s C_i^{*}-M_{snk,i}^{Bio}+M_{source,i}^{NAPL}=\theta R\frac{\partial C_i}{\partial t}$$

Advection

Dispersion

Fluid Source/Sink

Biodegradation Reaction Term

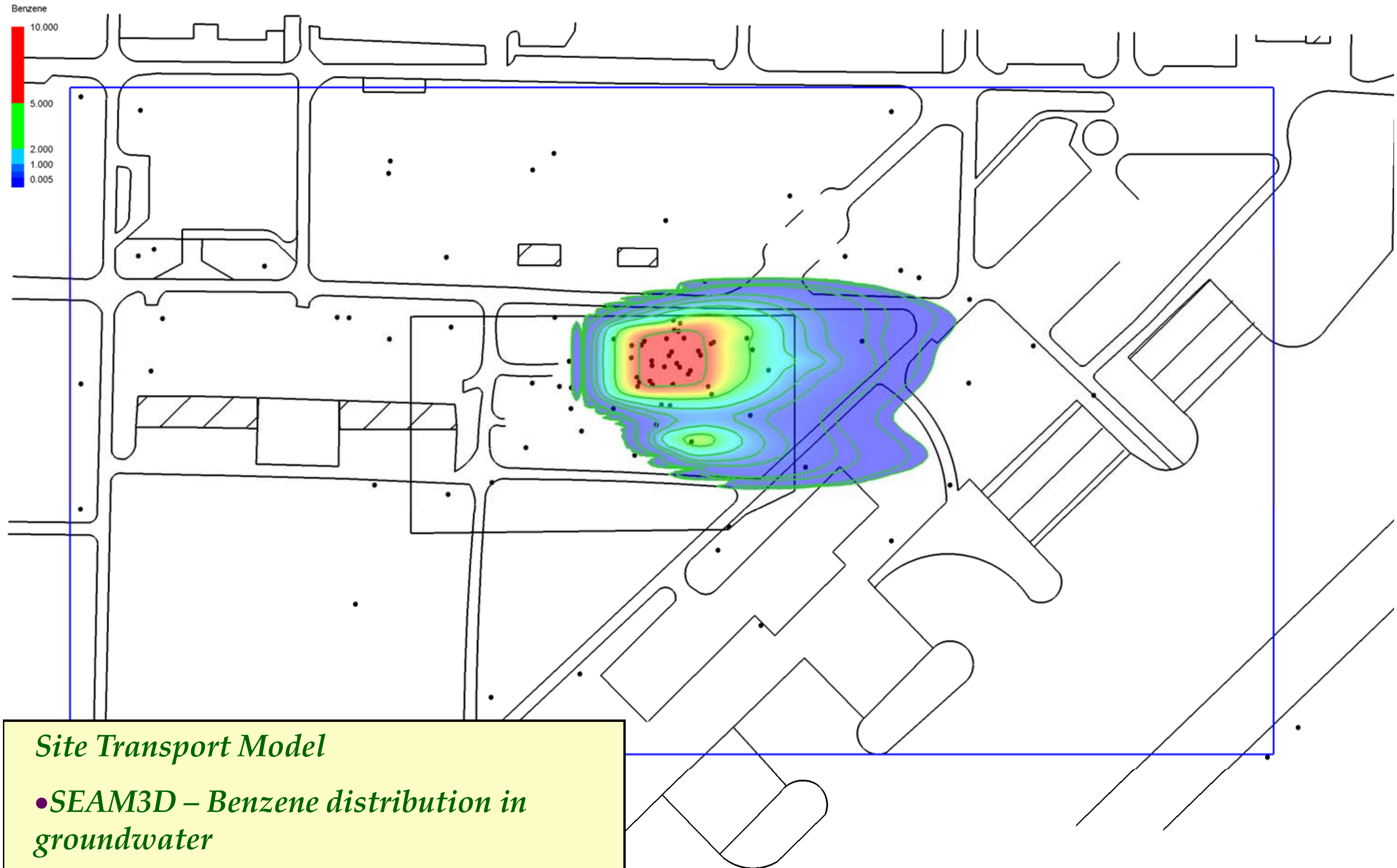
NAPL Dissolution Source Term

Retardation Factor

Biodegradation

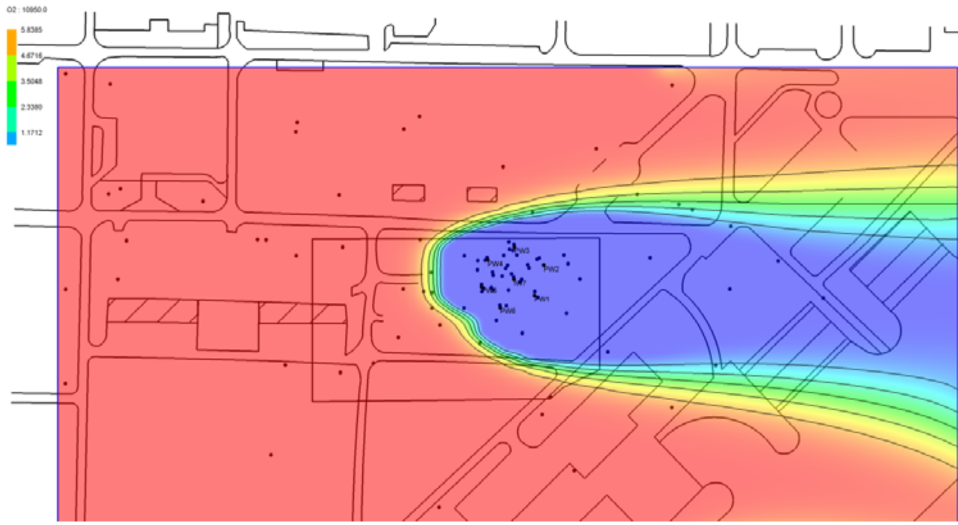
- Hydrocarbon Biodegradation Sink Term
  - Sum of all applicable terminal electron-accepting processes (TEAPs)
  - Utilization rates for compound, i (TEAP-specific)

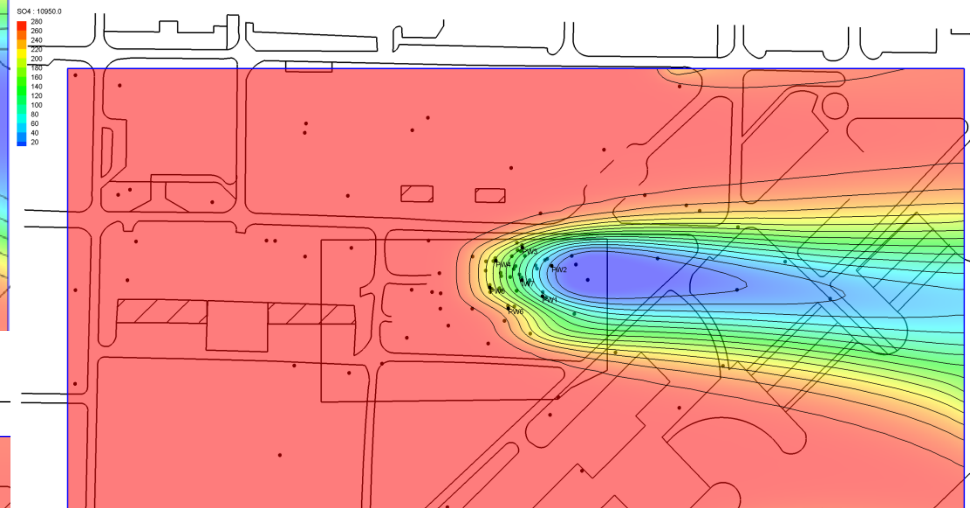
$$M_{snk,i}^{Bio} = \sum_{ea} v_{x,i,ea}^{\max} \left[\frac{C_i}{K_{x,i,ea}^{ed} + C_i} \right] \left[\frac{E_{ea}}{K_{x,le}^{ea} + E_{ea}} \right] I_{ea,li}$$

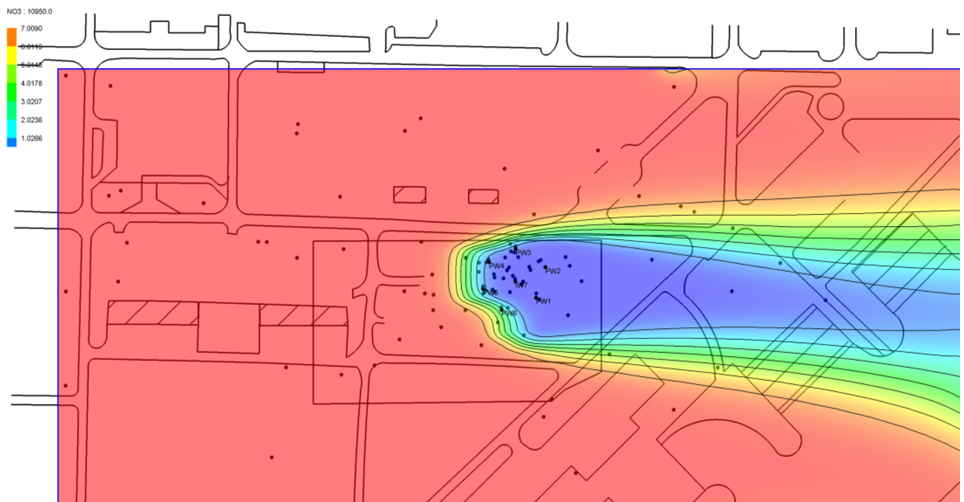


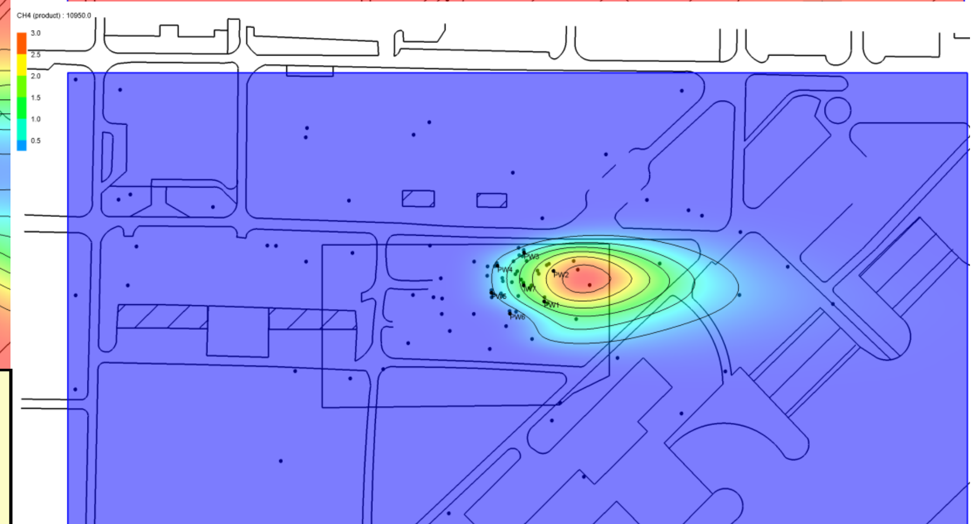
Site Transport Model

- *SEAM3D – Benzene distribution in groundwater*
- **Calibrated to current site conditions**









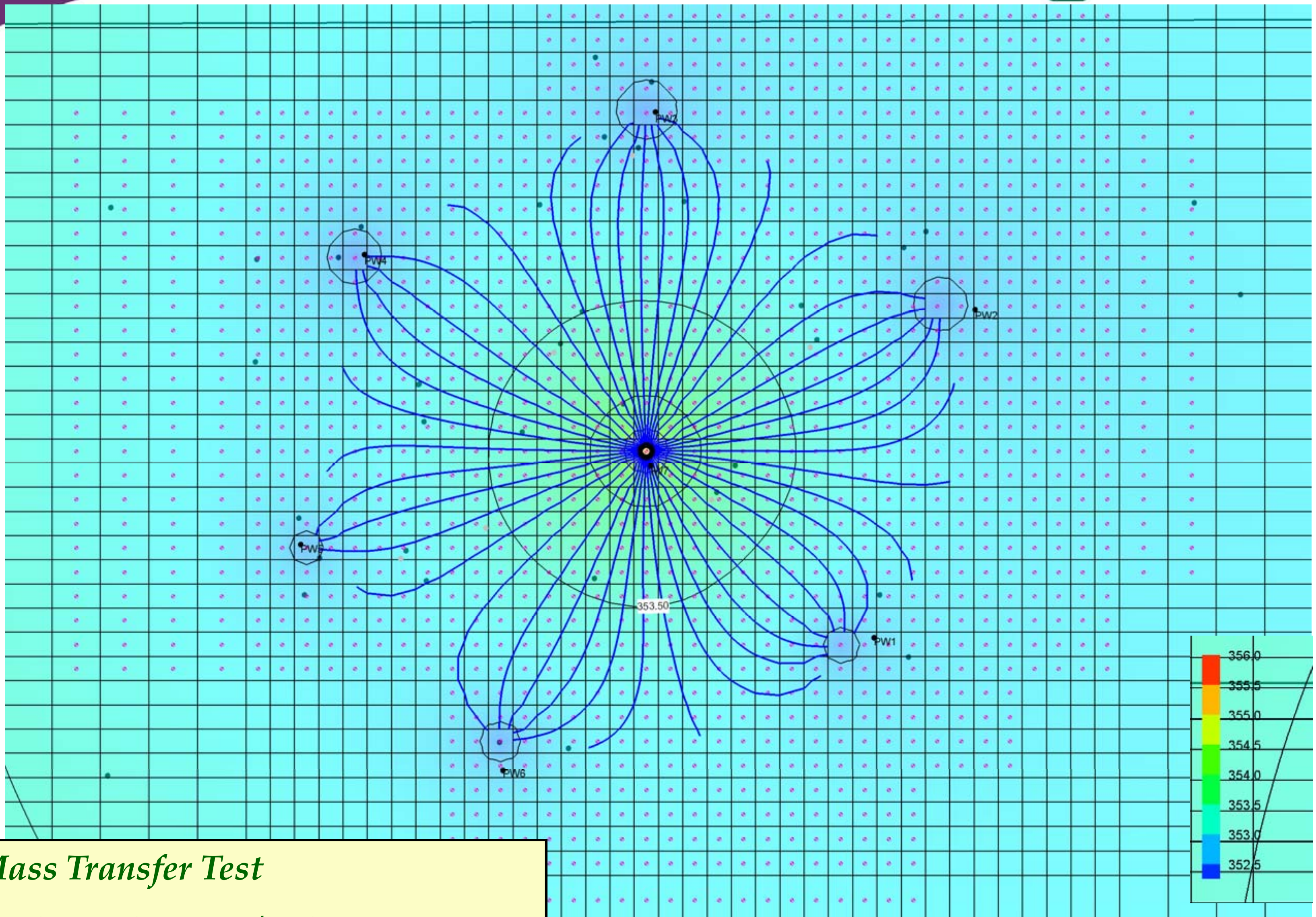
Site Transport Model – SEAM3D

•*Electron Acceptors (DO, NO_3, SO_4)*

•*Methane*

Model Validation - MTT

- Validation of the source zone model is accomplished by simulating the mass transfer test using MODFLOW and SEAM3D
- Steps
  - Improve resolution of model grid
  - Validate flow model
    - Injection/pumping data
    - Water level data
  - Refine NAPL mass estimates and mass transfer parameters
    - Estimates constrained by results of MTT data interpretation



Mass Transfer Test

- *MODFLOW2000/MODPATH*
- **Calibrated to Pre-TEE MTT**

Source Zone Model

- NAPL Dissolution – Hydrocarbon mass transfer is modeled using a first order mass transfer function:

$$M_{source,i}^{NAPL} = K(C_i^{eq} - C_i)$$

- K is a time-dependent mass transfer coefficient based on the upscaled mass transfer function

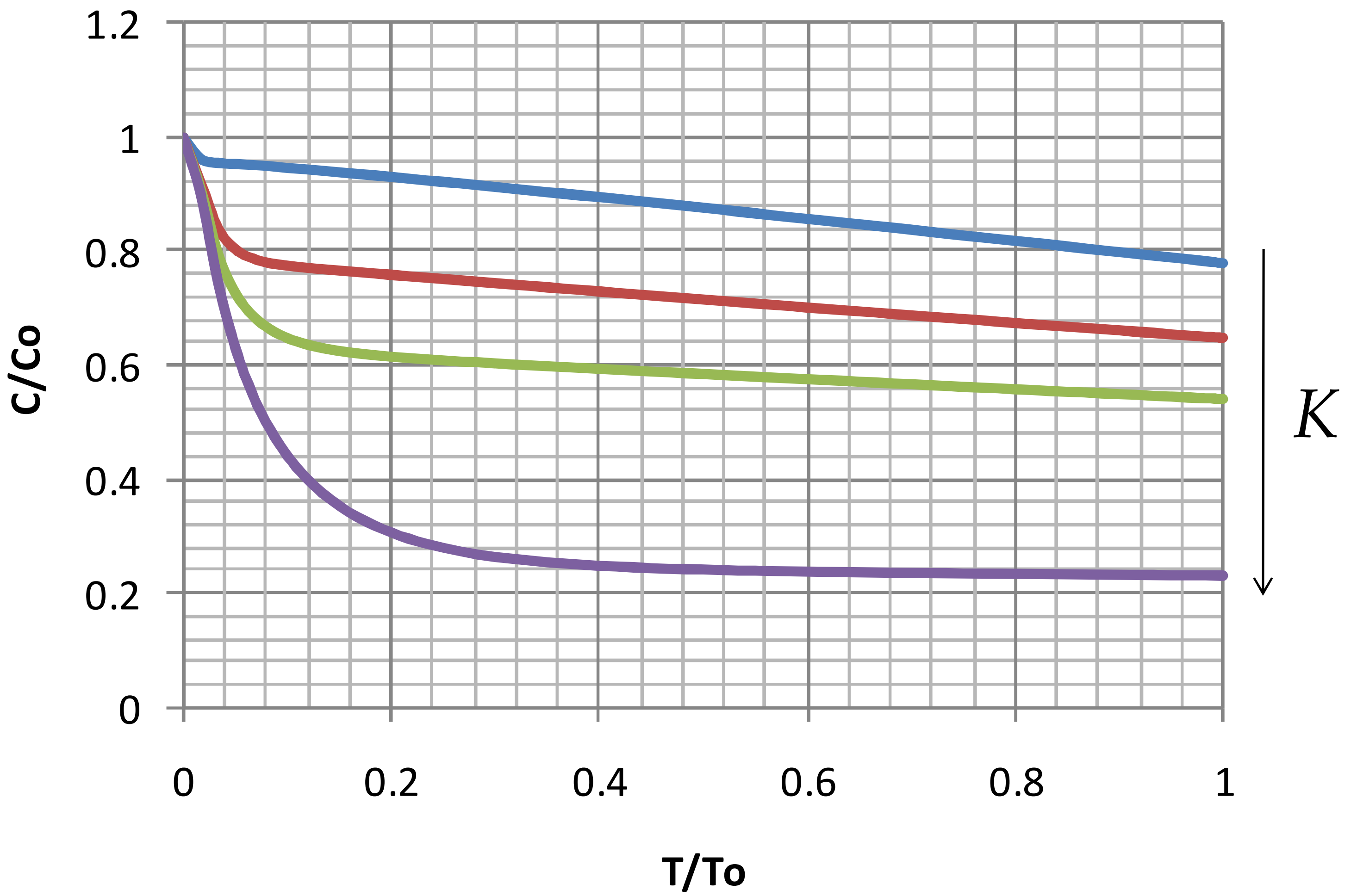
$$K(t) = k^{NAPL}\left(\frac{V}{V_o}\right)^{\Gamma}$$

  - V = volume of NAPL
  - k_{NAPL} = field-scale mass transfer coefficient
  - G = upscaled mass transfer parameter
  - C_i^{eq} = equilibrium aqueous concentration

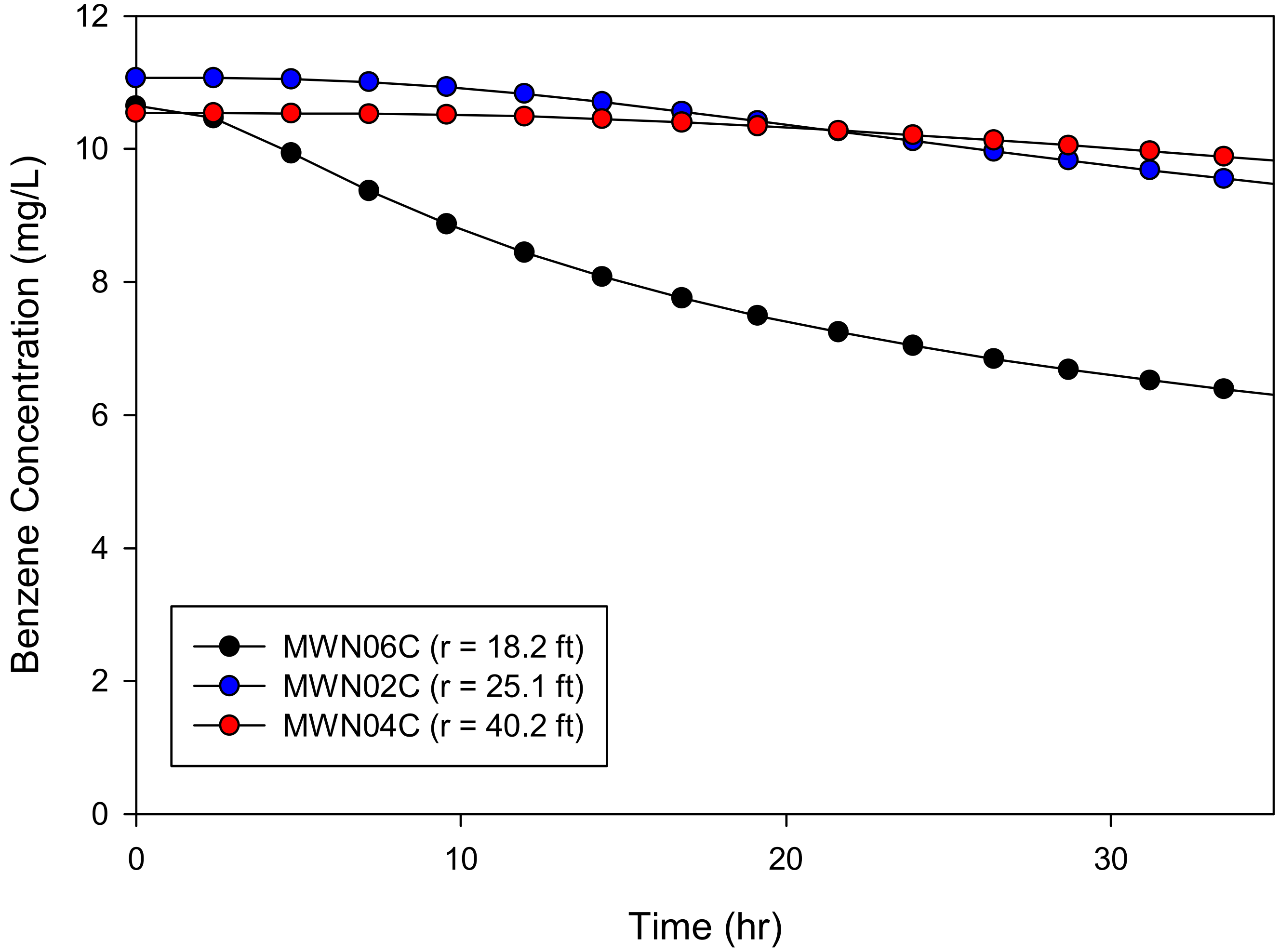
Source Model – Initial Parameter Estimates

- Calibrated STA model input parameters
- Pre-test monitoring well data – contaminant concentrations
  - NAPL source components – equilibrium concentrations
  - Composition of NAPL
- Results of MMT analysis
  - NAPL mass and distribution
  - Mass transfer rate

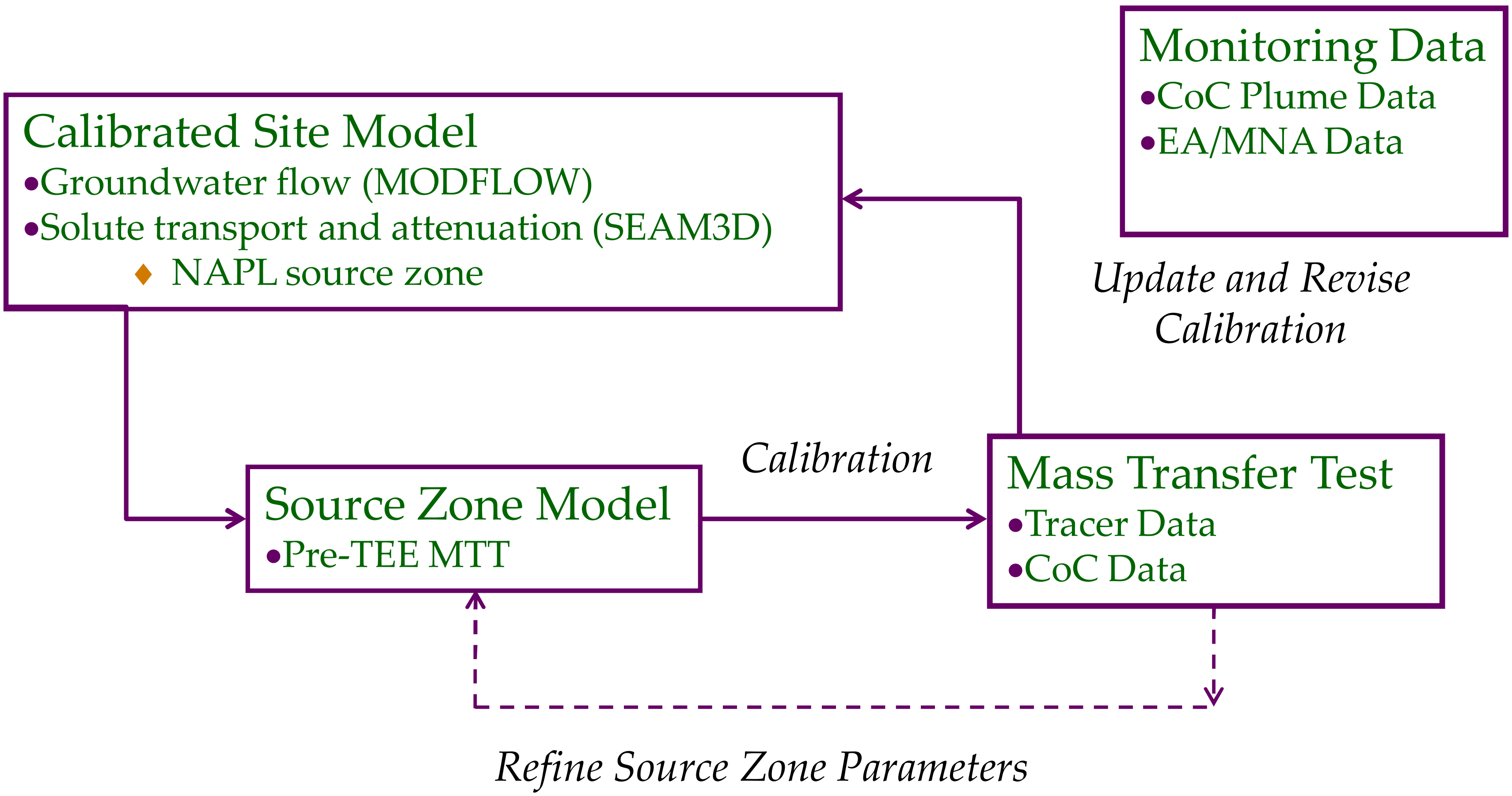
Breakthrough Curves (Pre-TEE)



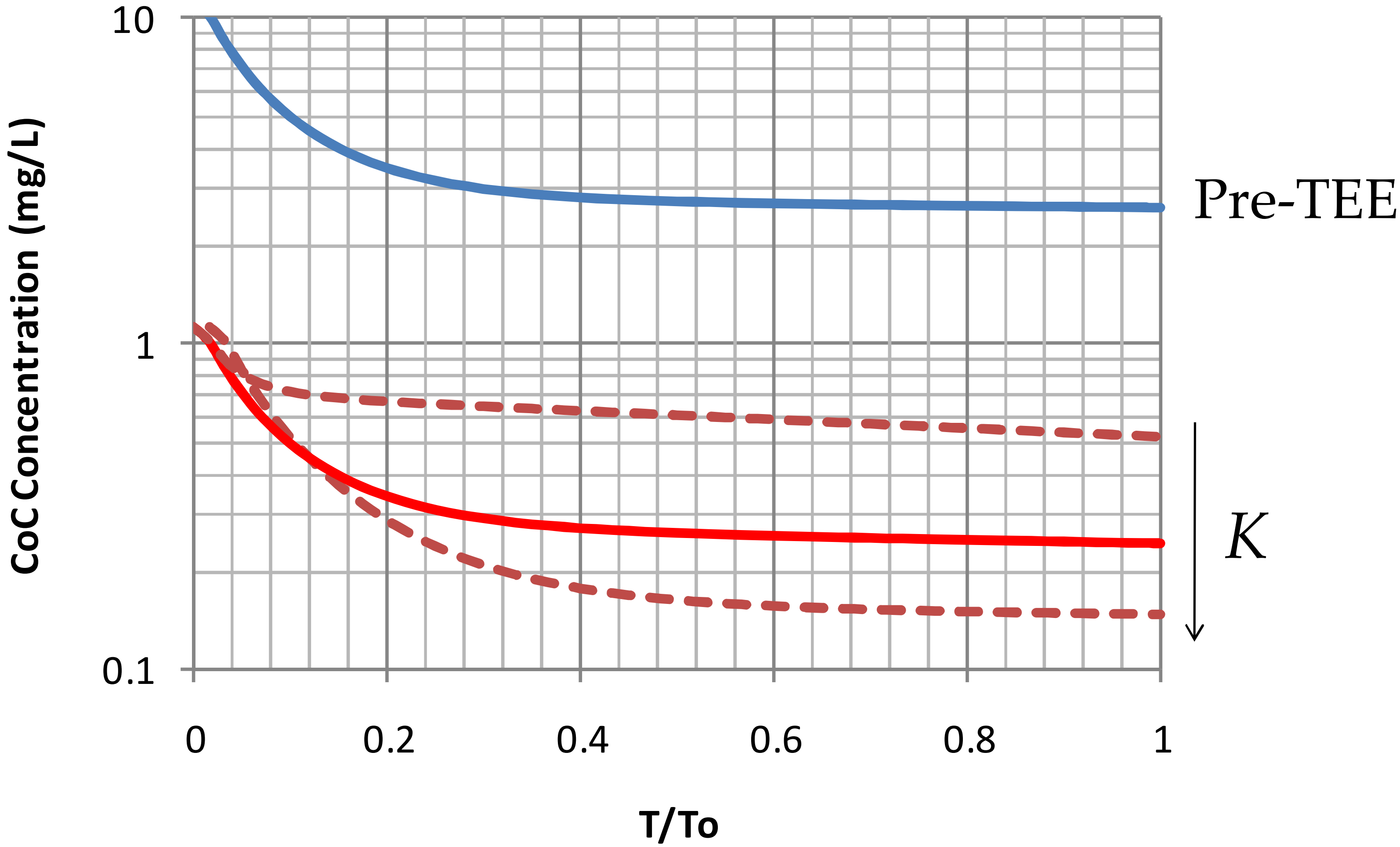
Breakthrough Curves (Pre-TEE)



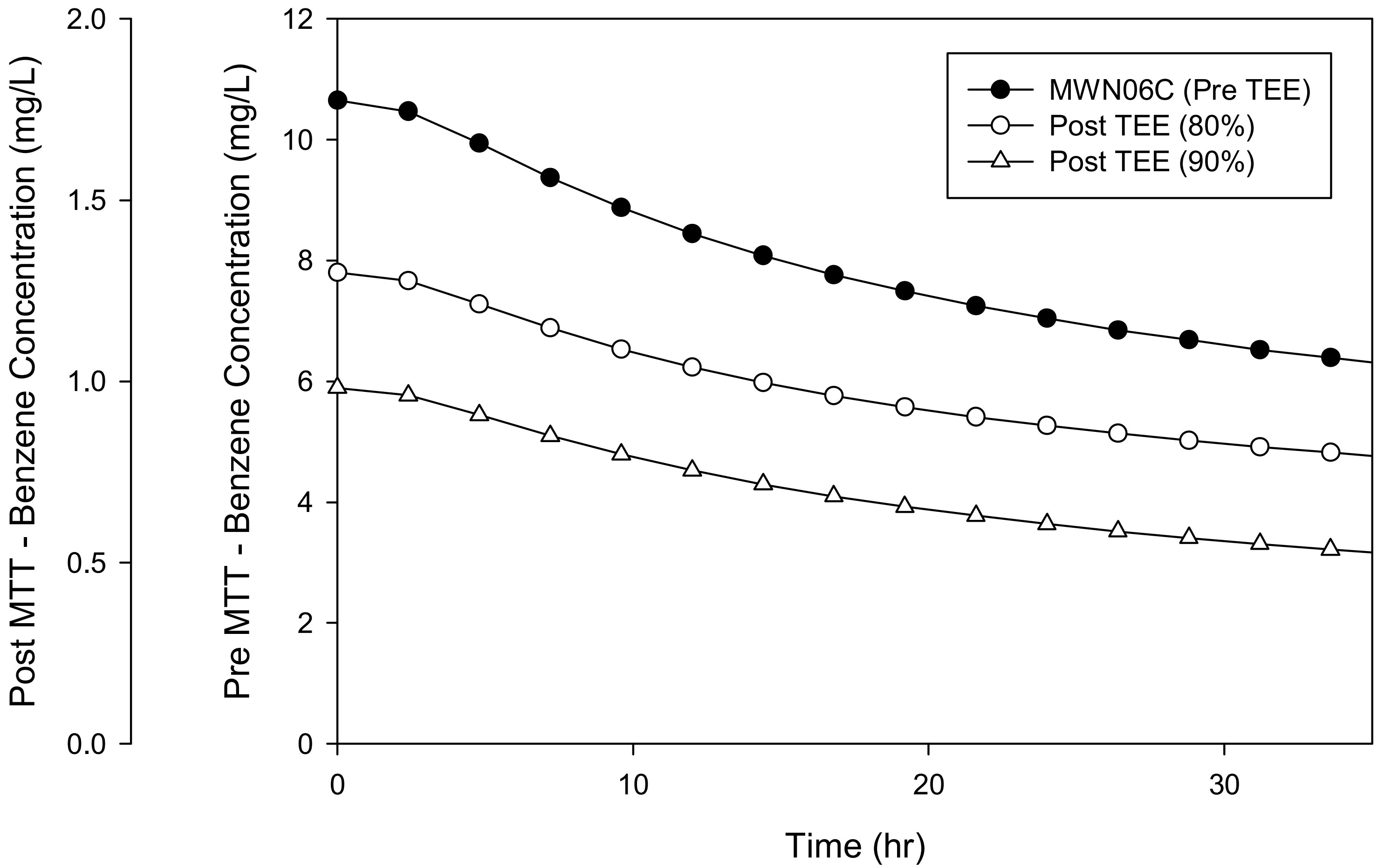
Source Model – Parameter Revision



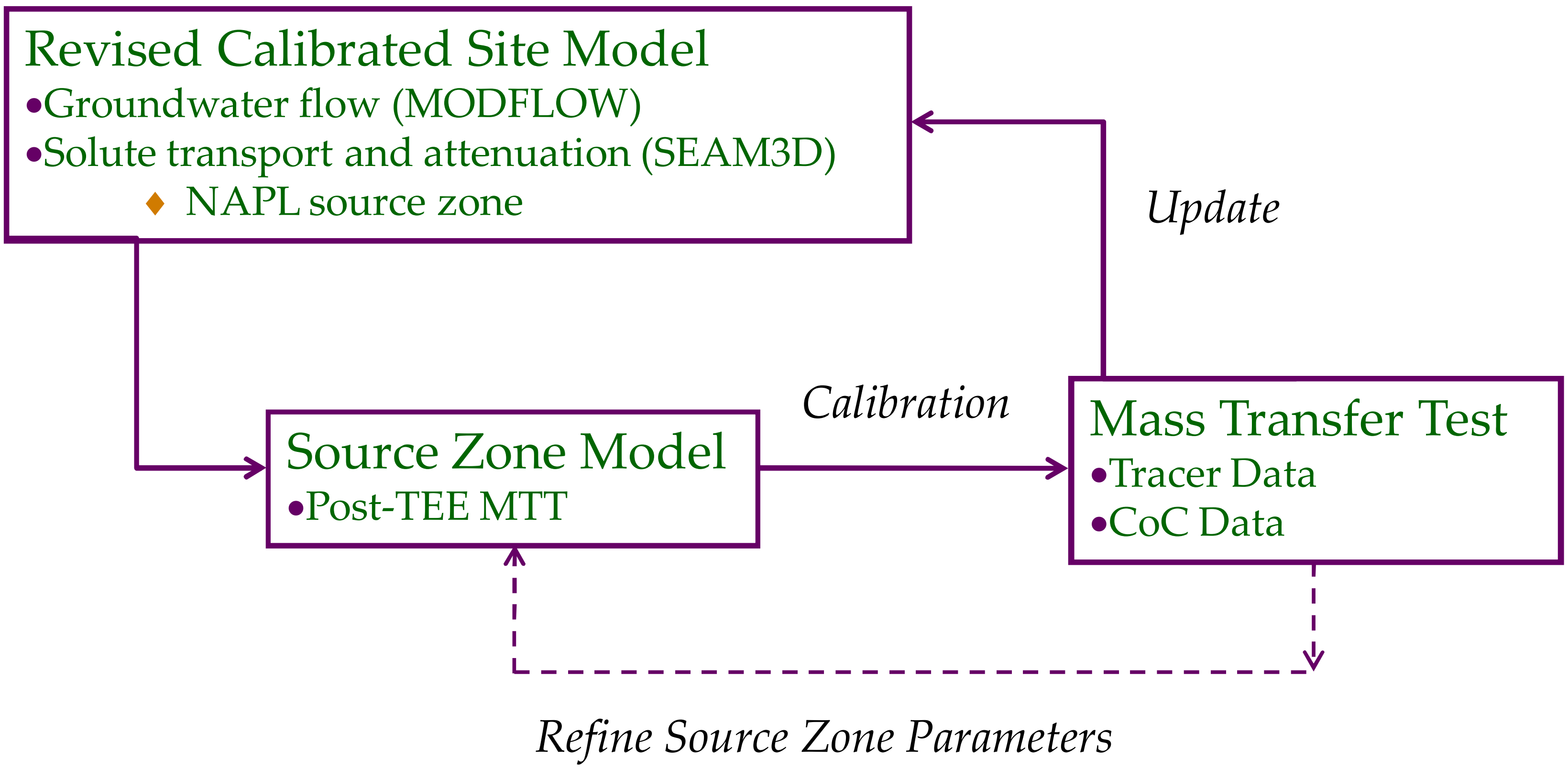
Breakthrough Curves (Post-TEE)



Breakthrough Curves (Post-TEE)

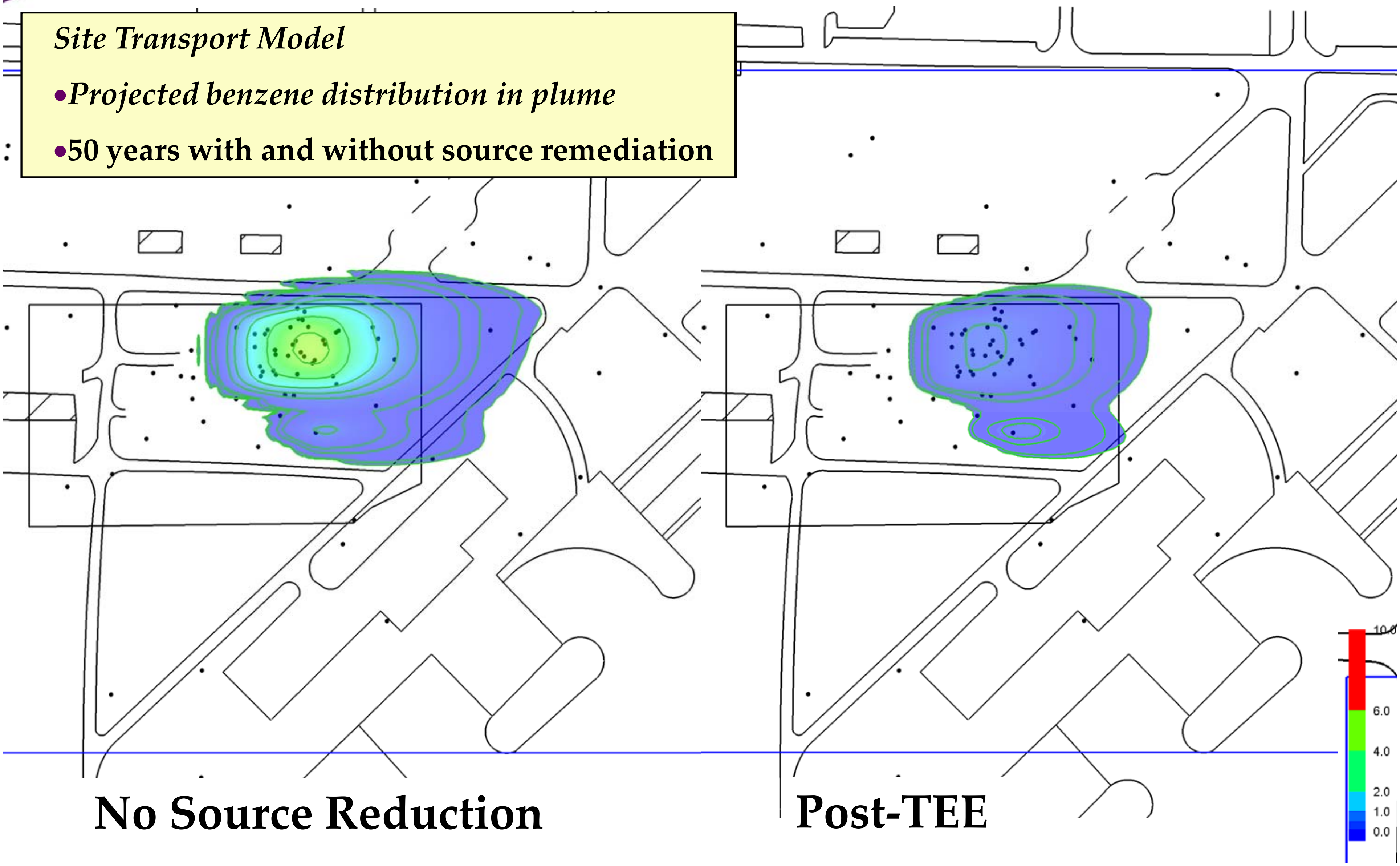


Source Model – Post Remediation



Site Transport Model

- ***Projected benzene distribution in plume***
- **50 years with and without source remediation**

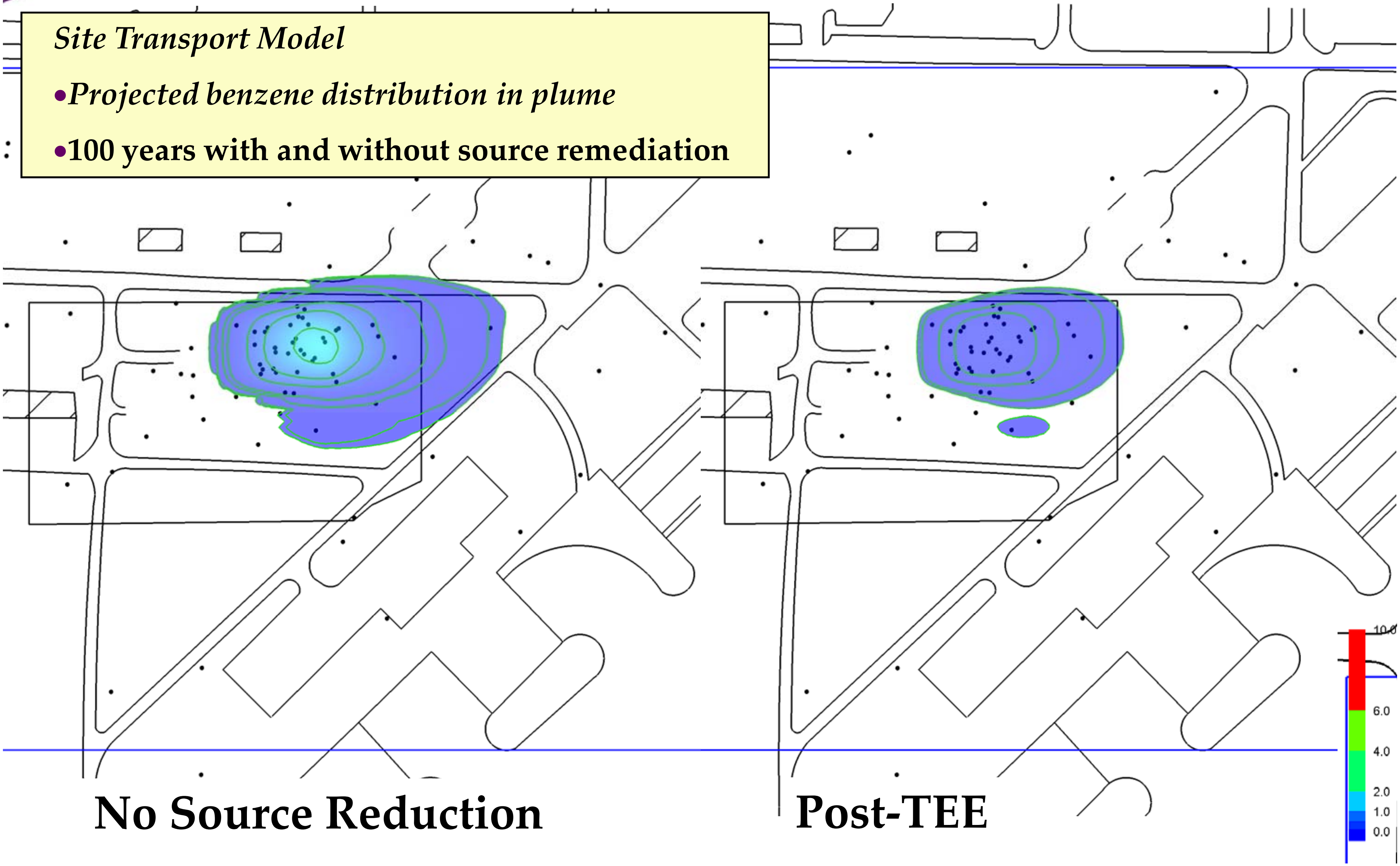


No Source Reduction

Post-TEE

Site Transport Model

- *Projected benzene distribution in plume*
- **100 years with and without source remediation**



No Source Reduction | **Post-TEE**

Conclusions: Decision-Making Tool for NAPL Source Zones

- Overview of tool
  - Combination of innovative field measurements and interpretation using a computational model
  - Measurement of mass dissolution rate from the source zone
  - Modeling source term to predict future mass dissolution rates and plume longevity
- Advantages
  - Testing and analytical tool for evaluating multiple scenarios for source zone reduction and plume longevity
  - Reduces uncertainty associated with remedial timeframe estimates – additional data collection constrains model input parameters that control source depletion and plume longevity

Conclusions: Decision-Making Tool for NAPL Source Zones (Continued)

- Limitations
  - Mass transfer coefficients may not be applicable across a site
    - Does the test accurately measure mass transfer from low permeability units?
  - Model predictions are dependent on NAPL mass estimates that may vary widely within the source zone
- Cost
  - Application of this tool will require a monetary investment
  - Cost saving may be realized by use of available test infrastructure

Short Course Agenda

8:30 AM	Welcome and Introduction	Hans Stroo
8:40 AM	Source Zone Protocol for Remedy Selection of Chlorinated Solvents Released at DoD Facilities	Thomas Sale & Charles Newell
9:50 AM	Break	
10:10 AM	Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation	Carmen Lebrón, Bernard Kueper, David Major, Julie Konzuk & Jason Gerhard
11:50 AM	Lunch	
1:00 PM	Decision & Management Tools for DNAPL Sites: Optimization of Chlorinated Solvent Source and Plume Remediation Considering Uncertainty	Ronald Falta & Charles Newell
2:20 PM	Emulsion Design Tool for Planning Aqueous Amendment Injections Systems	Robert Borden
2:20 PM	Break	
3:10 PM	Permanganate Design Tool for Planning Aqueous Amendment Injection Systems	Robert Borden
4:00 PM	Improved Field Evaluation of NAPL Dissolution and Source Longevity	Michael Kavanaugh, Mark Widdowson, Lloyd Stewart & Rula Deeb
5:20 PM	Summary & Conclusion	Hans Stroo